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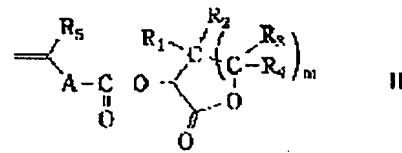
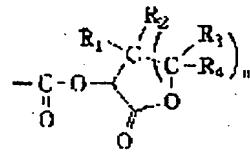
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(54) POSITIVE TYPE PHOTORESIST COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To improve adhesion to a substrate as well as to ensure satisfactory fitness for light in a short wavelength range, high sensitivity and superior resist pattern profile by incorporating a specified resin and a specified compd.

SOLUTION: This photoresist compsn. contains a resin having an ester group represented by formula I in each molecule and a compd. generating an acid when irradiated with active light or radiation. In formulae I, II each of R1-R4 may be same or different, is H or alkyl and (m) is 1 or 2. The resin is decomposed by the action of the acid to increase the solubility to an alkali soln. and contains repeating structural units corresponding to a monomer represented by formula II (where R5 is H or methyl and A is a single bond, alkylene, substd. alkylene, ether, thio-ether, carbonyl, ester, etc.).



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審査請求 未請求 請求項の数 4 O.L (全 28 頁)

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(22) 出願日 平成9年(1997)2月27日	(72) 発明者 佐藤 健一郎 静岡県榛原郡吉田町川尻4000番地 富士写 真フィルム株式会社内
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(54) 【発明の名称】 ポジ型フォトレジスト組成物

(57) 【要約】

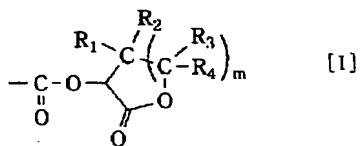
【課題】 170 nm～220 nmという波長領域の光に対して十分好適であり、かつ光に対して高感度で、得られるレジストパターンプロファイルが優れ、且つ基板との密着性が優れたポジ型フォトレジスト組成物を提供することにある。

【解決手段】 特定のエステル基を分子内に有し、且つ酸の作用により分解しアルカリ溶液に対する溶解性が増加する樹脂と活性光線または放射線の照射により酸を発生する化合物とを含有するポジ型フォトレジスト組成物。

【特許請求の範囲】

【請求項1】 下記一般式〔I〕で表されるエステル基を分子内に有し、且つ酸の作用により分解しアルカリ溶液に対する溶解性が増加する樹脂と、活性光線または放射線の照射により酸を発生する化合物とを含有することを特徴とするポジ型フォトレジスト組成物。

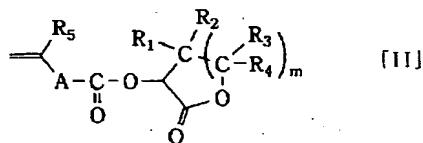
【化1】



(式中、R₁～R₄は、同じでも異なってもよく、水素原子又はアルキル基を表す。mは1又は2を表す。)

【請求項2】 前記樹脂が、下記一般式〔II〕で示される単量体に相当する繰り返し構造単位を含み、且つ酸の作用により分解しアルカリ溶液に対する溶解性が増加する樹脂であることを特徴とする請求項1に記載のポジ型フォトレジスト組成物。

【化2】



(式中、R₁～R₄及びmは請求項1に記載のものと同義である。R₅は水素原子またはメチル基を表す。Aは単結合、アルキレン基、置換アルキレン基、エーテル基、チオエーテル基、カルボニル基、エステル基、アミド基、スルファンアミド基、ウレタン基、ウレア基の中から選ばれる1つの基もしくはそれら2つ以上を組み合わせた基を表す。)

【請求項3】 前記樹脂が、更に脂肪族環状炭化水素部位を有する繰り返し構造単位を含むことを特徴とする請求項1または2に記載のポジ型フォトレジスト組成物。

【請求項4】 前記樹脂が、更に酸の作用により分解し、アルカリ現像液中の溶解性を増大させる基を有する繰り返し構造単位を含むことを特徴とする請求項1～3のいずれかに記載のポジ型フォトレジスト組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、活性光線または放射線、その中でも特に170nm～220nmという非常に波長の短い光で露光処理する場合に好適なポジ型フォトレジスト組成物に関し、詳しくは高感度で、優れたレジストパターンが得られ、且つ基板との密着性が優れたパターンが得られるポジ型フォトレジスト組成物に関するものである。

【0002】

【従来の技術】 近年、半導体素子等の微細加工を必要と

する各種電子デバイス製造の分野においては、デバイスのますますの高密度化、高集積化に関する要求が高まっている。これに伴いパターンの微細化を実現するためのフォトグラフィー技術に対する要求性能は厳しさを極めている。この微細化技術の一翼を担っているのがフォトレジストの高解像力化であり、また露光光の短波長化である。

【0003】 一般に、光学系の解像度(Res)はレーリーの式、すなわち $Res = k \cdot \lambda / NA$ (kはプロセスファクター、λは露光光源の波長、NAはレンズの開口数)で表すことができる。この式からより再現線幅を小さくし、微細なパターンを解像するためには(すなわち高解像力を得るために)、露光時の波長を短くすればよいことが分かる。確かに、最小再現線幅の縮小とともに露光波長は高圧水銀灯のg線(436nm)、i線(365nm)へと移行し、更にKrFエキシマレーザー(248nm)を使用したデバイス製造が検討されている。そして、更なる微細加工に対してはより短波なエキシマレーザー、中でもArF(193nm)の利用が有望視されている。

【0004】 短波長光で露光するフォトレジストの方に目を移すと、従来製造化につながってきた单層レジストではなく、表面リソグラフィーを利用した2層以上の多層レジスト系での高集積化も検討されている。しかし、これまで多層レジストの実用化を阻んできたプロセスの煩雑化は依然として問題である。また、KrFエキシマレーザーを始めとするエキシマレーザーの場合、ガス寿命が短いこと、そもそも露光装置自体が高価であるため、レーザーのコストパフォーマンスを高める必要があると一般にされている。

【0005】 これに答えたのがKrFエキシマレーザー露光用途から主流となつたいわゆる化学增幅型レジストである。化学增幅型レジストは露光により系内の触媒量存在する光酸発生剤から酸が発生し、その触媒量の酸によりバインダーあるいは低分子化合物のアルカリ可溶性基の保護基を触媒反応的に脱離させ、アルカリ現像液に対する溶解性のディスクリミネーションを確保するという仕組みである。化学增幅型レジストは光反応により発生した酸を触媒反応的に利用することから高感度化が期待できる。

【0006】 一般に化学增幅系レジストは、通称2成分系、2.5成分系、3成分系の3種類に大別することができる。2成分系は、光酸発生剤とバインダー樹脂とを組み合わせている。該バインダー樹脂は、酸の作用により分解して、樹脂のアルカリ現像液中の溶解性を増大させる基(酸分解性基ともいう)を分子内に有する樹脂である。2.5成分系はこうした2成分系に更に酸分解性基を有する低分子化合物を含有する。3成分系は光酸発生剤とアルカリ可溶性樹脂と上記低分子化合物を含有するものである。

【0007】しかしながら、露光光が短波長になると新たな問題が生じた。即ち、フォトレジストにおいて、波長の短い光に対して透明性がいい素材はドライエッティング耐性に支障がある。ドライエッティング耐性がいい素材は透明性が悪いという問題点である。ドライエッティング耐性と透明性の両立というのは基本的にはフォトレジスト層中のバインダー樹脂の性能の問題である。バインダーとしてはノボラック樹脂やポリp-ヒドロキシスチレンがある。ノボラック樹脂はi線レジスト用アルカリ可溶性樹脂として広い利用があり、ポリp-ヒドロキシスチレンはK.r.Fエキシマレーザーレジスト用のベースポリマーとして利用がある。これらは波長の長い光を使う限り大きな問題にはならない。波長の短い光の場合は異なる。特に、上記樹脂は、170nm～220nmという波長領域には高い光学濃度を有し、これらを從来同様に直接使用することは事実上不可能である。このため、高い光透明性を有し、かつドライエッティング耐性も高い樹脂の開発が待望された。

【0008】この問題に対する一般的な回答の一つには、樹脂に例えば脂肪族環状炭化水素部位を導入するという方法がある。また、芳香族化合物の一つナフタレン骨格を利用するという方法もある。特に、脂肪族環状炭化水素部位の導入により、光透明性とドライエッティング耐性という両方の要請を満たすことについては数々の報告例がある。たとえば、Journal of Photopolymer Science and technology vol. 3, p439, 1992.などがある。

【0009】一方、酸分解性基を含有する樹脂における酸分解性基として何を選択するかは特に、レジストの感度や解像度、さらに経時安定性をも左右するもので重要である。これまで、カルボン酸基類を保護する酸分解性基としてはt-ブチルエステル等の3級アルキルエステル類や、テトラヒドロピラニルエステル、エトキシエチルエステル等のアセタールエステル類が主に報告されている。しかし、t-ブチルエステル基は発生した酸による脱離能力が低く、感度が低下してしまうという難点がある。テトラヒドロピラニルエステル、エトキシエチルエステル等は逆に、常温でも分解しやすく、経時安定性に大きな問題を抱えていた。また、特開平5-346668号公報は3-オキソシクロヘキシルエステル基を酸分解性基として使用する提案を行っているが、感度の点で必ずしも満足がいく物ではなかった。このように、フォトレジストにおいて感度と経時保存安定性を同時に満足するカルボン酸類を保護した酸分解性基をどのように設計すればよいか必ずしも明確ではなかった。また、得られるレジストパターンにおいて、再現線幅を小さくし、微細なパターンを解像するためには、上記特性ばかりでなく、得られた微細なパターンの基板への十分な密着性が必要とされる。この密着性が不十分であると、微細なパターンが得られたとしてもそれが剥がれてしまうことがある。

【0010】

【発明が解決しようとする課題】よって、本発明の目的は、特に170nm～220nmという波長領域の光に対して十分好適であり、かつ光に対して高感度で、得られるレジストパターンプロファイルが優れ、且つ基板との密着性が優れたポジ型フォトレジスト組成物を提供することにある。

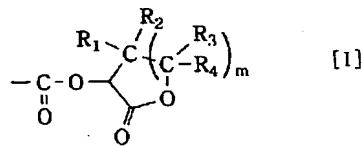
【0011】

【課題を解決するための手段】本発明者らは上記諸特性に留意して鋭意検討した結果、特定の構造を有する基を有する樹脂を用いることにより上記目的が見事に解決されることを見だし、本発明に至った。即ち、上記目的は下記の構成により達成できる。

(1) 下記一般式〔I〕で表されるエステル基を分子内に有し、且つ酸の作用により分解しアルカリ溶液に対する溶解性が増加する樹脂と、活性光線または放射線の照射により酸を発生する化合物とを含有することを特徴とするポジ型フォトレジスト組成物。

【0012】

【化3】

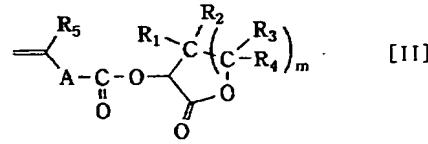


【0013】(式中、R₁～R₄は、同じでも異なってもよく、水素原子又はアルキル基を表す。mは1又は2を表す。)

(2) 前記樹脂が、下記一般式〔II〕で示される単量体に相当する繰り返し構造単位を含み、且つ酸の作用により分解しアルカリ溶液に対する溶解性が増加する樹脂であることを特徴とする前記(1)に記載のポジ型フォトレジスト組成物。

【0014】

【化4】



【0015】(式中、R₁～R₄及びmは前記(1)に記載のものと同義である。R₅は水素原子またはメチル基を表す。Aは単結合、アルキレン基、置換アルキレン基、エーテル基、チオエーテル基、カルボニル基、エステル基、アミド基、スルファンアミド基、ウレタン基、ウレア基の中から選ばれる1つの基もしくはそれら2つ以上を組み合わせた基を表す。)

(3) 前記樹脂が、更に脂肪族環状炭化水素部位を有する繰り返し構造単位を含むことを特徴とする前記

(1) または(2)に記載のポジ型フォトレジスト組成

物。

(4) 前記樹脂が、更に酸の作用により分解し、アルカリ現像液中の溶解性を増大させる基を有する繰り返し構造単位を含むことを特徴とする前記(1)～(3)のいずれかに記載のポジ型フォトレジスト組成物。

【0016】

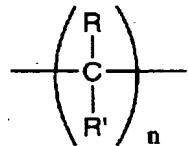
【発明の実施の形態】以下、本発明を詳細に説明する。一般式〔I〕中のR₁～R₄が示すアルキル基としては、メチル基、エチル基、プロピル基、イソプロピル基、ブチル基、イソブチル基、sec-ブチル基等の低級アルキル基が好ましく、より好ましくはメチル基、エチル基、プロピル基、イソプロピル基、ブチル基であり、更に好ましくはメチル基、エチル基である。mは1又は2を表し、好ましくは1である。

【0017】上記一般式〔I〕で示される基を含む樹脂における母体樹脂としては、本発明の効果が得られるものであればいずれのものでもよい。本発明においては、一般式〔I〕で示される基を含む樹脂としては、上記一般式〔II〕で示される単量体に相当する繰り返し構造単位を含む樹脂が好ましい。この樹脂は、例えば上記一般式〔II〕で示される単量体をラジカル重合することで得ることができる。

【0018】上記一般式〔II〕中のAとしては、単結合または、アルキレン基、置換アルキレン基、エーテル基、チオエーテル基、カルボニル基、エステル基、アミド基、スルファンアミド基、ウレタン基、ウレア基の中から選んだ1つの基もしくは2つ以上組み合わせた基である。Aのアルキレン基、置換アルキレン基としては、下記で示される基を挙げることができる。

【0019】

【化5】

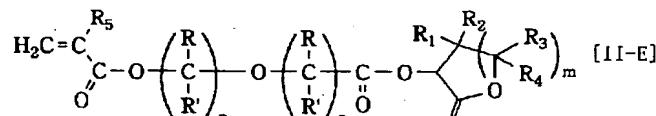
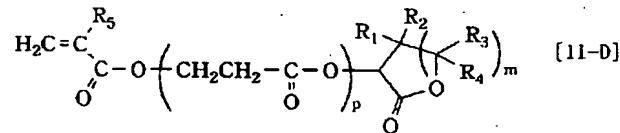
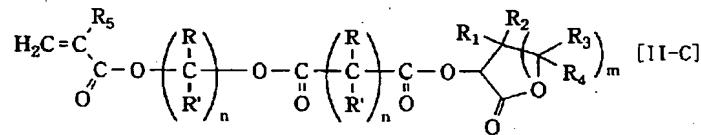
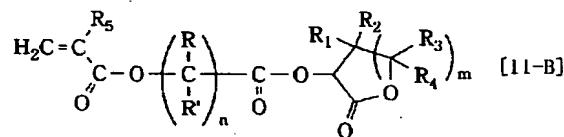
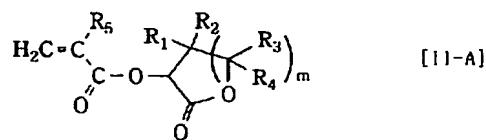


【0020】R、R'：水素原子、アルキル基、置換アルキル基、ハロゲン原子、水酸基又はアルコキシ基を表し、両者は同一でも異なっていてもよい。ここでアルキル基としては、メチル基、エチル基、プロピル基、イソプロピル基、ブチル基等の低級アルキル基が好ましく、更に好ましくはメチル基、エチル基、プロピル基、又はイソプロピル基である。置換アルキル基としては、水酸基、ハロゲン原子、アルコキシ基を挙げができる。アルコキシ基としては、メトキシ基、エトキシ基、プロポキシ基、ブトキシ基等の炭素数1～4個のものを挙げができる。nは1～10の整数を表す。

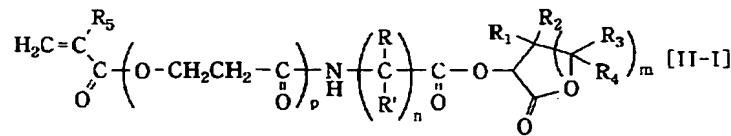
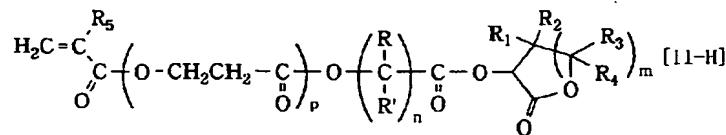
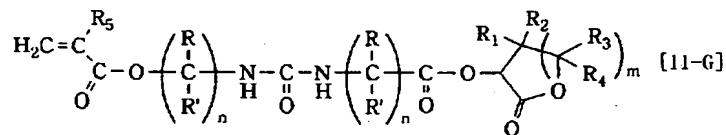
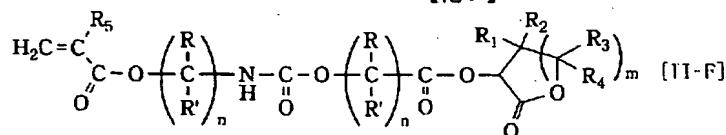
【0021】Aとしては上記の中でも、単結合または、アルキレン基、置換アルキレン基、エーテル基、エステル基、アミド基、ウレタン基、ウレア基の中から選んだ1つの基もしくは2つ以上組み合わせた基が特に好ましい。ここで、アルキレン基、置換アルキレン基としては、炭素数1～4個のアルキレン基が好ましく、具体的にはメチレン基、エチレン基、プロピレン基、ブチレン基、メチル置換メチレン基、ジメチル置換メチレン基、メチル置換エチレン基、ジメチル置換エチレン基、メチル置換プロピレン基、ジメチル置換プロピレン基が挙げられる。以下に一般式〔II〕で示される単量体の内好ましいものとしては、一般式〔II-A〕～〔II-I〕で表される単量体を挙げができる。

【0022】

【化6】

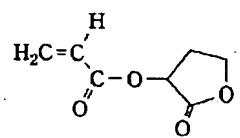


【0023】



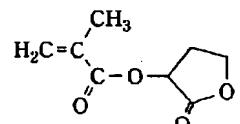
【0024】上記一般式において、R₁～R₅、R、R'、n、mは、各々上記と同義である。pは1～3の数を表す。以下に一般式 (II) で示される単量体の具体例を示す。ただし、これらは本発明の内容を限定するものではない。

【0025】
【化8】

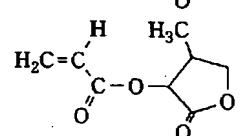


[III-A-1]

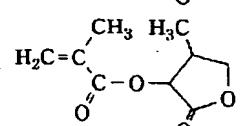
【0026】
【化9】



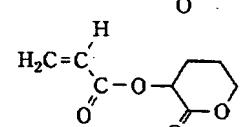
[III-A-2]



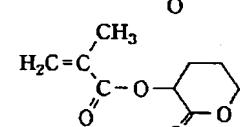
[III-A-3]



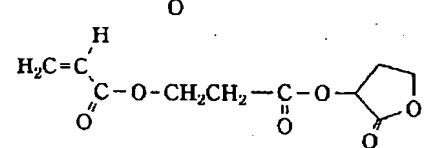
[III-A-4]



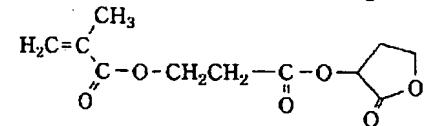
[III-A-5]



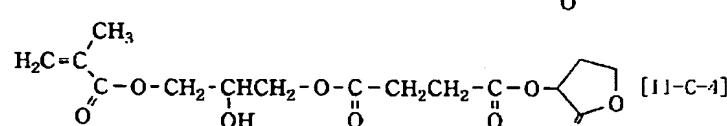
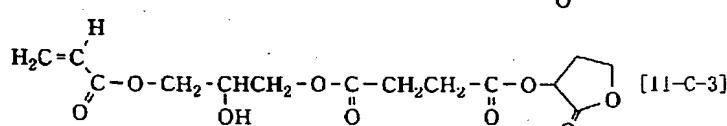
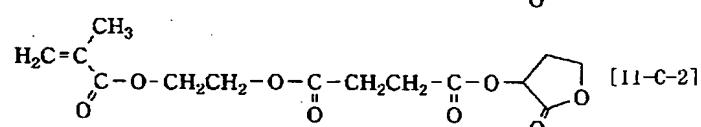
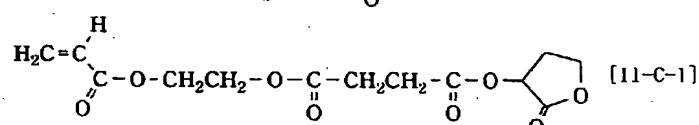
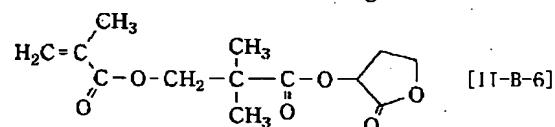
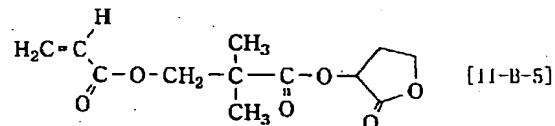
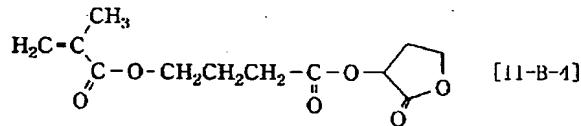
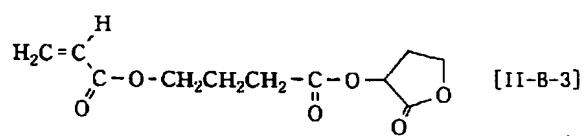
[III-A-6]



[II-B-1]

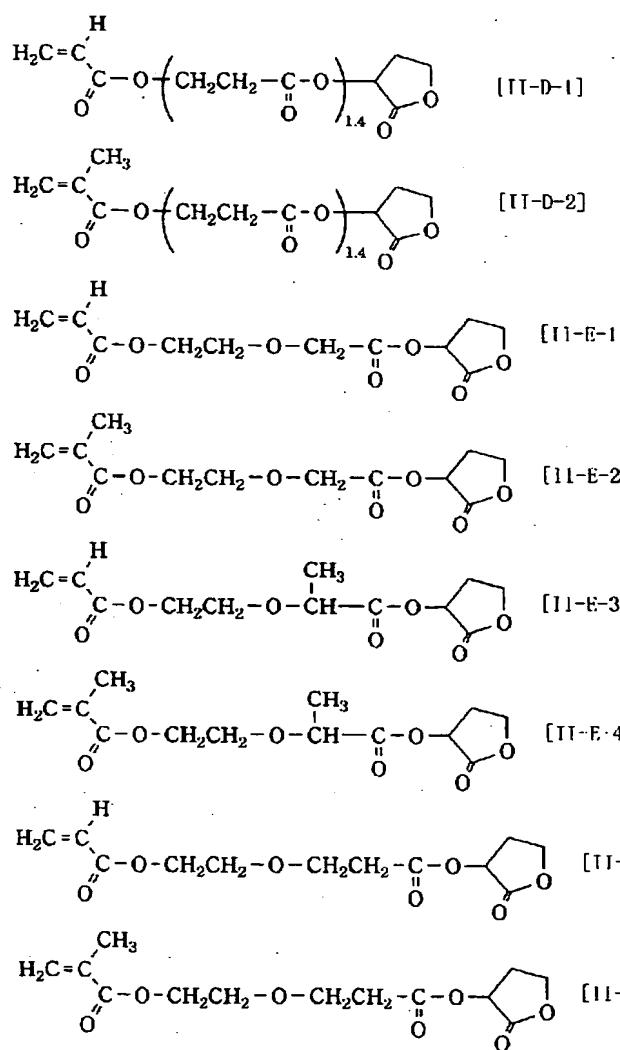


[II-B-2]



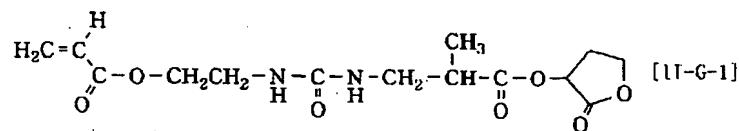
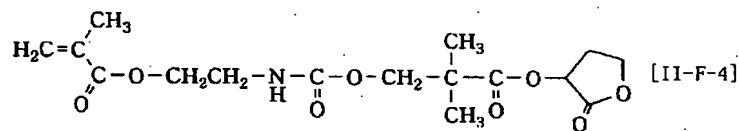
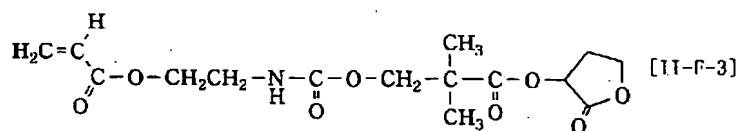
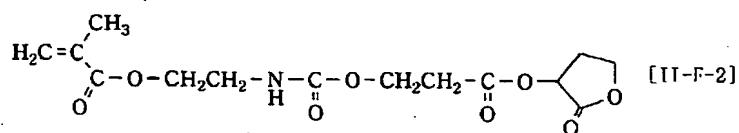
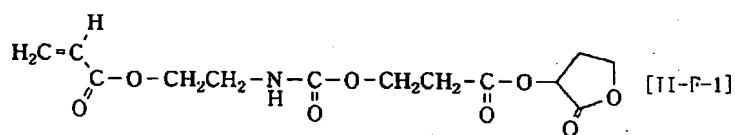
【0027】

【化10】



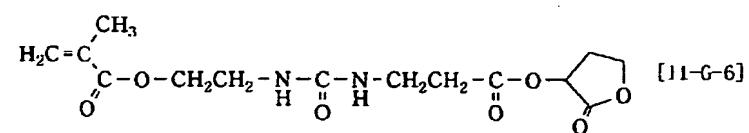
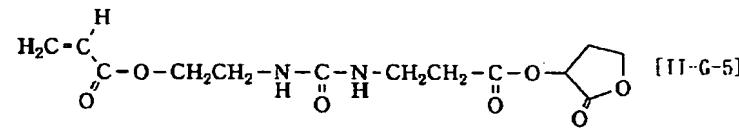
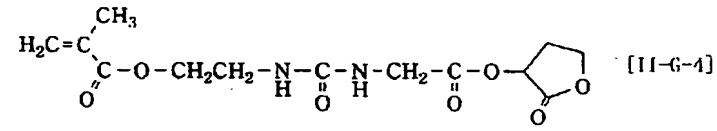
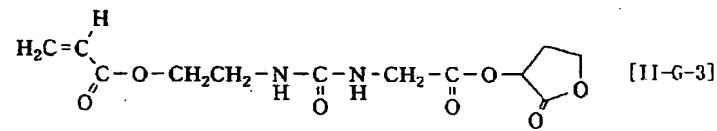
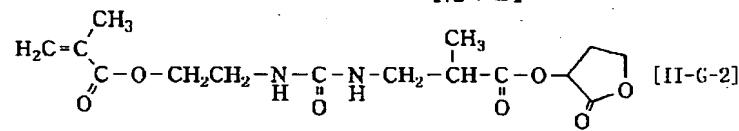
【0028】

【化11】



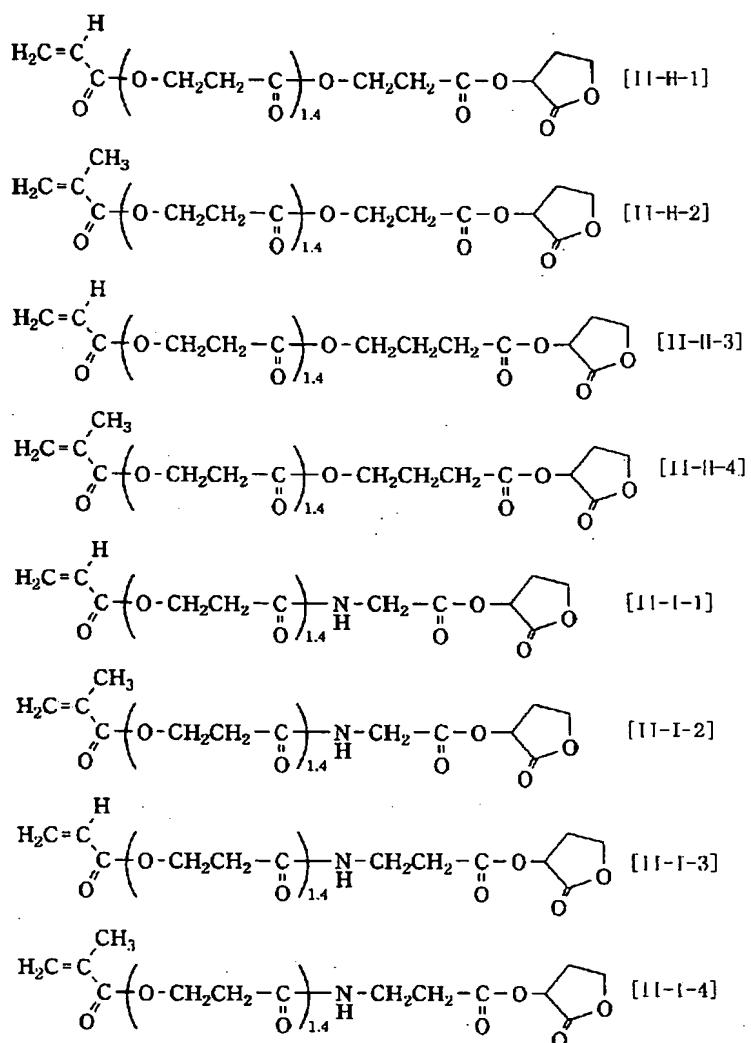
[0029]

【化 1 2】



[0030]

【化 1 3】

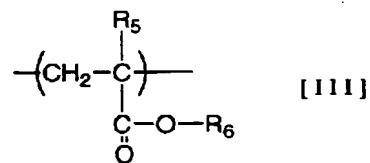


【0031】このような一般式〔II〕で示される単量体は、ラジカル重合可能な炭素-炭素二重結合を分子内に有するカルボン酸類と2-ヒドロキシラクトン類をAngew. Chem. int. Ed. Engl., 1978, 17, 522に記載の方法でエステル化、あるいは対応するカルボン酸クロリドと2-ヒドロキシラクトン類を塩基性条件下反応させることにより合成できる。

【0032】本発明のポジ型フォトレジスト組成物における樹脂は、上記一般式〔I〕で示される基とともに、分子内に脂肪族環状炭化水素部位を有する繰り返し構造単位を含むことが好ましい。これにより、ポジ型フォトレジストのドライエッキング耐性を高めることができ。分子内に脂肪族環状炭化水素部位を有する繰り返し構造単位としては、例えば下記一般式〔III〕あるいは〔IV〕で示される繰り返し構造単位を挙げることができる。

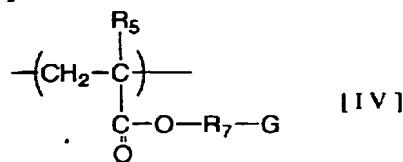
【0033】

【化14】



【0034】

【化15】

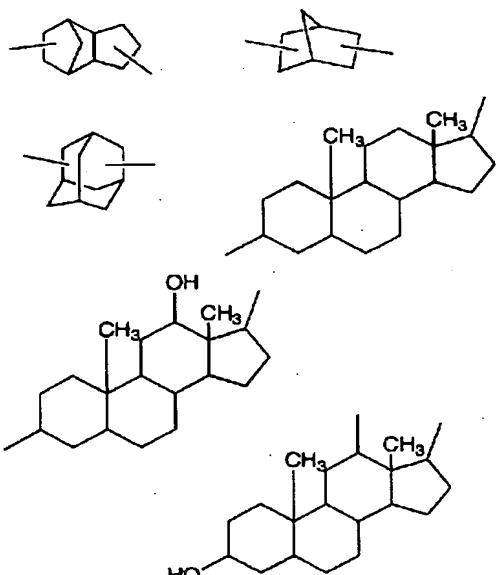


【0035】一般式〔III〕中のR₆は1価の脂肪族環状炭化水素基である。具体的には、アダマンチル基、2-メチル-2-アダマンチル基、ノルボルニル基、ボロニル基、イソボロニル基、トリシクロデカニル基、ジシクロペンテニル基、ノボルナンエポキシ基、メンチル基、

イソメンチル基、ネオメンチル基等を挙げることができる。一般式 [IV] 中、R₇ は2価の脂肪族環状炭化水素部位を有する連結基である。Gは、-COOH、-O H、-COOR₈ 又は-OR₈ を表す。R₈ は3級アルキル基、テトラヒドロピラニル基、テトラヒドロフラニル基、-CH₂ OR₉ 又は-CH(CH₃) OR₉ を表す。R₉ はアルキル基を表す。R₅ は前記と同義である。R₇ の連結基中に含まれる脂肪族環状炭化水素部位としては、例えば以下のような構造を挙げができる。

【0036】

【化16】



【0037】また、上記脂肪族環状炭化水素部位とエステル基、あるいは上記脂肪族環状炭化水素部位とG基をつなぐR₇ 内の連結基としては単結合でもよく、アルキレン基、エーテル基、チオエーテル基、カルボニル基、エステル基、アミド基、スルファンアミド基等の中から選ばれる1つの基もしくは2つ以上を組み合わせた基を挙げができる。

【0038】-COOR₈ 基もしくは-OR₈ 基におけるR₈ は、t-ブチル基、t-アミル基等の3級アルキル基、テトラヒドロピラニル基、テトラヒドロフラニル基、-CH(CH₃) OCH₂ CH₃ 基、-CH(CH₃) OCH₂ CH(CH₃)₂ 基等の1-アルコキシエチル基、-CH₂ OCH₃ 基、-CH₂ OCH₂ CH₃ 基等のアルコキシメチル基等の酸の作用により分解する置換基を表す。

【0039】上記樹脂中、一般式 [I] で示される基を含む繰り返し構造単位の含有率は、全繰り返し単位に対して3モル%~60モル%が好ましく、より好ましくは5モル%~50モル%である。3モル%未満の場合は本発明の効果が発現しにくく好ましくない。60モル%を越えるとドライエッティング耐性が劣化しやすくなつて好

ましくない。分子内に脂肪族環状炭化水素部位を有する繰り返し構造単位の樹脂中の含有量は、全繰り返し単位に対して97~40モル%が好ましく、より好ましくは95~50モル%である。

【0040】上記本発明に係わる樹脂は、更に一般式 [I] で示される基、脂肪族環状炭化水素部位を有する繰り返し構造単位以外に、酸の作用により分解し、アルカリ現像液中で溶解性を増大させる基（酸分解性基ともいう）を含有することが好ましい。これにより、感度向上効果が一層顕著になる。このような酸分解性基としては、上記-COOR₈、-OR₈、3-オキソシクロヘキシル基、又は2-オキソシクロヘキシル基が好ましい。具体的には、次のような既存の単量体に相当する繰り返し構造単位が挙げられる。

【0041】例えば、t-ブチルアクリレート、t-ブチルメタクリレート、t-アミルアクリレート、t-アミルメタクリレート、テトラヒドロフラニルアクリレート、テトラヒドロフラニルメタクリレート、テトラヒドロピラニルアクリレート、テトラヒドロピラニルメタクリレート、アルコキシメチルアクリレート、アルコキシメチルメタクリレート、1-アルコキシエチルメタクリレート、3-オキソシクロヘキシルアクリレート、3-オキソシクロヘキシルメタクリレート、2-オキソシクロヘキシルアクリレート、2-オキソシクロヘキシルメタクリレートなどを挙げができる。

【0042】上記の樹脂中、このような既存の酸分解性基を有する単量体に基づく繰り返し構造単位の含有率においては、既存の酸分解性基/上記一般式 [I] で示される基を有する繰り返し構造単位=6/1以下が好ましく、更に好ましくは3/1以下である。該値が6/1を越えると本発明の効果が十分に発現しないため好ましくない。

【0043】このような樹脂は、本発明の効果が有效地に得られる範囲内で、更に以下のような単量体を繰り返し単位として共重合させることができるが、これらに限定されるものではない。これにより、前記樹脂に要求される性能、特に（1）塗布溶剤に対する溶解性、（2）製膜性（ガラス転移点）、（3）アルカリ現像性、（4）膜ベリ（親疎水性、アルカリ可溶性基選択）、（5）未露光部の基板への密着性、（6）ドライエッティング耐性、の微調整が可能となる。

【0044】このような共重合単量体としては、例えば、アクリル酸エステル類、メタクリル酸エステル類、アクリルアミド類、メタクリルアミド類、アリル化合物、ビニルエーテル類、ビニルエステル類等から選ばれる付加重合性不飽和結合を1個有する化合物などを挙げることができる。

【0045】具体的には、例えばアクリル酸エステル類、例えばアルキル（アルキル基の炭素原子数は1~10のものが好ましい）アクリレート（例えば、アクリル

酸メチル、アクリル酸エチル、アクリル酸プロピル、アクリル酸アミル、アクリル酸シクロヘキシル、アクリル酸エチルヘキシル、アクリル酸オクチル、アクリル酸-t-オクチル、クロルエチルアクリレート、2-ヒドロキシエチルアクリレート2, 2-ジメチルヒドロキシプロピルアクリレート、5-ヒドロキシペンチルアクリレート、トリメチロールプロパンモノアクリレート、ペンタエリスリトールモノアクリレート、ベンジルアクリレート、メトキシベンジルアクリレート、フルフリルアクリレート、テトラヒドロフルフリルアクリレートなど) ;

【0046】メタクリル酸エステル類、例えばアルキル(アルキル基の炭素原子数は1~10のものが好ましい。)メタクリレート(例えばメチルメタクリレート、エチルメタクリレート、プロピルメタクリレート、イソプロピルメタクリレート、アミルメタクリレート、ヘキシルメタクリレート、シクロヘキシルメタクリレート、ベンジルメタクリレート、クロルベンジルメタクリレート、オクチルメタクリレート、2-ヒドロキシエチルメタクリレート、4-ヒドロキシブチルメタクリレート、5-ヒドロキシペンチルメタクリレート、2, 2-ジメチル-3-ヒドロキシプロピルメタクリレート、トリメチロールプロパンモノメタクリレート、ペンタエリスリトールモノメタクリレート、フルフリルメタクリレート、テトラヒドロフルフリルメタクリレートなど) ;

【0047】アクリルアミド類、例えばアクリルアミド、N-アルキルアクリルアミド、(アルキル基としては炭素原子数1~10のもの、例えばメチル基、エチル基、プロピル基、ブチル基、t-ブチル基、ヘプチル基、オクチル基、シクロヘキシル基、ヒドロキシエチル基などがある。)、N, N-ジアルキルアクリルアミド(アルキル基としては炭素原子数1~10のもの、例えばメチル基、エチル基、ブチル基、イソブチル基、エチルヘキシル基、シクロヘキシル基などがある。)、N-ヒドロキシエチル-N-メチルアクリルアミド、N-2-アセトアミドエチル-N-アセチルアクリルアミドなど;

【0048】メタクリルアミド類、例えばメタクリルアミド、N-アルキルメタクリルアミド(アルキル基としては炭素原子数1~10のもの、例えばメチル基、エチル基、t-ブチル基、エチルヘキシル基、ヒドロキシエチル基、シクロヘキシル基などがある。)、N, N-ジアルキルメタクリルアミド(アルキル基としてはエチル基、プロピル基、ブチル基などがある。)、N-ヒドロキシエチル-N-メチルメタクリルアミドなど;

【0049】アリル化合物、例えばアリルエステル類

(例えば酢酸アリル、カプロン酸アリル、カプリル酸アリル、ラウリン酸アリル、パルミチン酸アリル、ステアリン酸アリル、安息香酸アリル、アセト酢酸アリル、乳酸アリルなど)、アリルオキシエタノールなど;

【0050】ビニルエーテル類、例えばアルキルビニルエーテル(例えばヘキシルビニルエーテル、オクチルビニルエーテル、デシルビニルエーテル、エチルヘキシルビニルエーテル、メトキシエチルビニルエーテル、エトキシエチルビニルエーテル、クロルエチルビニルエーテル、1-メチル-2, 2-ジメチルプロピルビニルエーテル、2-エチルブチルビニルエーテル、ヒドロキシエチルビニルエーテル、ジエチレングリコールビニルエーテル、ジメチルアミノエチルビニルエーテル、ジエチルアミノエチルビニルエーテル、ブチルアミノエチルビニルエーテル、ベンジルビニルエーテル、テトラヒドロフルフリルビニルエーテルなど) ;

【0051】ビニルエステル類、例えばビニルブチレート、ビニルイソブチレート、ビニルトリメチルアセテート、ビニルジエチルアセテート、ビニルバレート、ビニルカプロエート、ビニルクロルアセテート、ビニルジクロアセテート、ビニルメトキシアセテート、ビニルブトキシアセテート、ビニルアセトアセテート、ビニルラクトート、ビニル-β-フェニルブチレート、ビニルシクロヘキシカルボキシレートなど;

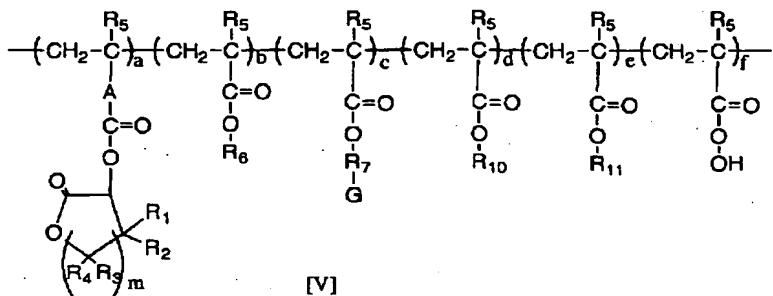
【0052】イタコン酸ジアルキル類(例えばイタコン酸ジメチル、イタコン酸ジエチル、イタコン酸ジブチルなど) ;マレイン酸あるいはスマール酸のジアルキルエステル類(例えばジメチルマレート、ジブチルスマール酸等)又はモノアルキルエステル類;アクリル酸、メタクリル酸、クロトン酸、イタコン酸、無水マレイン酸、マレイミド、アクリロニトリル、メタクリロニトリル、マレイロニトリル等がある。その他にも、一般式

〔I〕が表す基を含む繰り返し単位と共重合可能である付加重合性の不飽和化合物であればよい。上記のような更なる単量体に基づく繰り返し単位の樹脂中の含有量は、一般式〔I〕で示される繰り返し構造単位と脂肪族環状炭化水素部位を有する繰り返し構造単位の総モル数に対して99モル%以下が好ましく、より好ましくは90モル%以下、さらに好ましくは80モル%以下である。99モル%を越えると本発明の効果が十分に発現しないため好ましくない。

【0053】上記の樹脂としては例えば以下のよう一般式〔V〕で示すことができる。しかし、本発明の内容がこれに限定されるものではない。

【0054】

【化17】



【0055】上記式〔V〕中、R₁～R₇、A、Gは前記と同義である。

R₁₀：3級アルキル基、テトラヒドロピラニル基、テトラヒドロフラニル基、アルコキシエチル基、アルコキシメチル基、3-オキソシクロヘキシル基、2-オキソシクロヘキシル基を表す。

R₁₁：メチル基、エチル基、プロピル基、iso-プロピル基又はn-ブチル基を表す。

a : 5～80

b : 0～70

c : 0～95

d, e, f : 各々0～50

a+d≥5、b+c≥40、a+d≥5、a+b+c+d+e+f=100

を表す。

【0056】上記本発明に係わる樹脂の重量平均分子量は好ましくは、2,000～200,000である。重量平均分子量が2,000未満では耐熱性やドライエッティング耐性の劣化が見られるため余り好ましくなく、200,000を越えると現像性が劣化したり、粘度が極めて高くなるため製膜性が劣化するなど余り好ましくない結果を生じる。

【0057】本発明に係わる樹脂は、アゾ化合物などを開始剤とするラジカル重合をはじめとする通常の方法により合成できる。本発明のポジ型フォトレジスト組成物は、主として上記のような樹脂と光酸発生剤を含む。上記のような樹脂の組成物全体中の添加量は、全レジスト固形分中40～99重量%、好ましくは50～97重量%である。

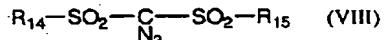
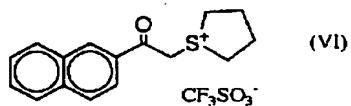
【0058】次に、本発明のポジ型フォトレジスト組成物における光酸発生剤について説明する。光酸発生剤は2つの性質を満たすことが必要である。すなわち、

(1) 露光光に対する透明性(但し、光ブリーチ性がない場合)と、(2) レジスト感度を確保するための十分な光分解性である。しかし、このような矛盾する必要要素を満たす分子設計指針は明確でないのが現状であるが、例えば次のような例を挙げることができる。すなわち、特開平7-25846号公報、特開平7-28237号公報、特開平7-92675号公報、特開平8-27102号公報に記載の2-オキソシクロヘキシル基を有する脂肪族アルキルスルfonyum塩類、および、N-

ヒドロキシスクシンイミドスルフォネート類などを挙げることができる。さらには J. Photopolym. Sci. Technol., Vol 7, No3, p 423 (1994) 等に記載があり、下記一般式(VI)で示すことができるスルfonyum塩、下記一般式(VII)で示すことができるジスルファン類、下記一般式(VIII)で表される化合物などを挙げができる。

【0059】

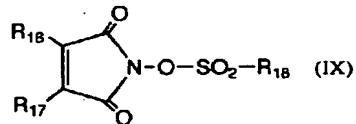
【化18】



【0060】ここで、R₁₂～R₁₅は各々アルキル基、環状アルキル基を表す。これらは互いに同じでも異なってもよい。また、下記一般式(IX)で示されるN-ヒドロキシマレインイミドスルフォネート類も好適である。

【0061】

【化19】



【0062】ここでR₁₆、R₁₇は、同じでも異なってもよく、水素原子、炭素数1～6個のアルキル基またはシクロアルキル基を表す。R₁₆とR₁₇とがアルキレン基を介して結合し、環を形成してもよい。R₁₈は、アルキル基、ペルフルオロアルキル基、シクロアルキル基または樟脑置換体を表す。このようなN-ヒドロキシマレインイミドスルフォネート類は光感度の点で特に好ましい。

【0063】上記一般式(IX)におけるR₁₆、R₁₇における炭素数1～6個のアルキル基としては、メチル基、エチル基、プロピル基、イソプロピル基、n-ブチル基、イソブチル基、tert-ブチル基、n-ペンチル基、n-ヘキシル基を挙げることができる。中でも好ましい

のはメチル基、エチル基、プロピル基であり、メチル基、エチル基が更に好ましい。炭素数6個以下のシクロアルキル基としてはシクロプロピル基、シクロペンチル基、シクロヘキシル基を挙げることができる。好ましくはシクロペンチル基、シクロヘキシル基である。R₁₆、R₁₇がアルキレン鎖により互いに環を形成する場合としては、例えばシクロヘキシル基、ノルボルニル基、トリシクロデカニル基を形成する場合などを挙げができる。

【0064】R₁₈のアルキル基としてはメチル基、エチル基、プロピル基を始めとする直鎖状の炭素数1～20個のアルキル基や、イソプロピル基、イソブチル基、tert-ブチル基、ネオペンチル基を始めとする分岐した炭素数1～20個のアルキル基を挙げができる。好ましくは炭素数1～16個の直鎖あるいは分岐したアルキル基であり、さらに好ましくは炭素数4～15個の直鎖あるいは分岐したアルキル基である。ペルフルオロアルキル基としては、トリフルオロメチル基、ペンタフルオロエチル基を始めとする直鎖の炭素数1～20個のペルフルオロアルキル基や、ヘプタフルオロイソブロピル基、ノナフルオロtert-ブチル基を始めとする分岐した炭素数1～20個のペルフルオロアルキル基を挙げができる。好ましくは炭素数1～16個の直鎖あるいは分岐したペルフルオロアルキル基である。環状のアルキル基としてはシクロペンチル基、シクロヘキシル基の様な単環状の環状のアルキル基や、デカリル基、ノルボルニル基、トリシクロデカニル基のような複数環状のアルキル基を挙げができる。

【0065】このような光酸発生剤の組成物中の添加量は、ポジ型フォトレジスト組成物の全固形分中、0.1～20重量%が好ましく、より好ましくは0.5～15重量%、更に好ましくは1～1.0重量%である。

【0066】本発明のポジ型フォトレジスト組成物には、上記のような光酸発生剤以外にも、以下のような光酸発生剤を併用してもよい。

【0067】以下のような併用可能な光酸発生剤の組成物中の添加量は、ポジ型フォトレジスト組成物全体の固形分中で2重量%以下であり、更に好ましくは1重量%以下がよい。たとえば S. I. Schlesinger, Photogr. Sci. Eng., 18, 387(1974)、T. S. Bal et al, Polymer, 21, 423(1980) 等に記載のジアゾニウム塩、米国特許第4,069,055号、同4,069,056号、同Re 27,992号、特願平3-140,140号等に記載のアンモニウム塩、D. C. Necker et al, Macromolecules, 17, 2468(1984)、C. S. Wen et al, Teh, Proc. Conf. Rad. Curing ASIA, p478 Tokyo, Oct(1988)、米国特許第4,069,055号、同4,069,056号等に記載のホスホニウム塩、J. V. Crivello et al, Macromolecules, 10(6), 1307(1977)、Chem. & Eng. News, Nov. 28, p31(1988)、欧州特許第104,143号、米国特許第339,049号、同第410,201号、特開平2-150,848号、特開平2-296,514号等に記載

のヨードニウム塩、J. V. Crivello et al, Polymer J. 17, 73(1985)、J. V. Crivello et al, J. Org. Chem., 43, 3055(1978)、W. R. Watt et al, J. Polymer Sci., Polymer Chem. Ed., 22, 1789(1984)、J. V. Crivello et al, Polymer Bull., 14, 279(1985)、J. V. Crivello et al, Macromolecules, 14(5), 1141(1981)、J. V. Crivello et al, J. Polymer Sci., Polymer Chem. Ed., 17, 2877(1979)、欧州特許第370,693号、同3,902,114号、同233,567号、同297,443号、同297,442号、米国特許第4,933,377号、同161,811号、同410,201号、同339,049号、同4,760,013号、同4,734,444号、同2,833,827号、獨国特許第2,904,626号、同3,604,580号、同3,604,581号等に記載のスルホニウム塩、J. V. Crivello et al, Macromolecules, 10(6), 1307(1977)、J. V. Crivello et al, J. Polymer Sci., Polymer Chem. Ed., 17, 1047(1979)等に記載のセレノニウム塩、C. S. Wen et al, Teh, Proc. Conf. Rad. Curing ASIA, p478 Tokyo, Oct(1988)等に記載のアルソニウム塩等のオニウム塩、米国特許第3,905,815号、特公昭46-4605号、特開昭48-36281号、特開昭55-32070号、特開昭60-239736号、特開昭61-169835号、特開昭61-169837号、特開昭62-58241号、特開昭62-212401号、特開昭63-70243号、特開昭63-298339号等に記載の有機ハロゲン化合物、K. Meier et al, J. Rad. Curing, 13(4), 26(1986)、T. P. Gillet et al, Inorg. Chem., 19, 3007(1980)、D. Astruc, Acc. Chem. Res., 19(12), 377(1896)、特開平2-161445号等に記載の有機金属／有機ハロゲン化合物、S. Hayase et al, J. Polymer Sci., 25, 753(1987)、E. Reichmanis et al, J. Polymer Sci., Polymer Chem. Ed., 23, 1(1985)、Q. Q. Zhu et al, J. Photochem., 36, 85, 39, 317(1987)、B. Amit et al, Tetrahedron Lett., (24) 2205(1973)、D. H. R. Barton et al, J. Chem. Soc., 3571(1965)、P. M. Collins et al, J. Chem. Soc., Perkin I, 1695(1975)、M. Rudinsteiner et al, Tetrahedron Lett., (17), 1445(1975)、J. W. Walker et al, J. Am. Chem. Soc., 110, 7170(1988)、S. C. Busman et al, J. Imaging Technol., 11(4), 191(1985)、H. M. Houlihan et al, Macromolecules, 21, 2001(1988)、P. M. Collins et al, J. Chem. Soc., Chem. Commun., 532(1972)、S. Hayase et al, Macromolecules, 18, 1799(1985)、E. Reichmanis et al, J. Electrochem. Soc., Solid State Sci. Technol., 130(6)、F. M. Houlihan et al, Macromolecules, 21, 2001(1988)、欧州特許第0290,750号、同046,083号、同156,535号、同271,851号、同0,388,343号、米国特許第3,901,710号、同4,181,531号、特開昭60-198538号、特開昭53-133022号等に記載のo-二トロベンジル型保護基を有する光酸発生剤、M. TUNOOKA et al, Polymer Preprints Japan, 35(8)、G. Berner et al, J. Rad. Curing, 13(4)、W. J. Mijs et al, Coating Technol., 55(697), 45(1983)、Akzo、H. Adachi et al, Polymer Preprints, Japan, 37(3)、欧州特許第0199,672号、同84515号、同199,672号、同044,115号、同0101,122号、米国特許第618,564号、同4,371,605号、同4,431,774

号、特開昭64-18143号、特開平2-245756号、特願平3-140109号等に記載のイミノスルフォネート等に代表される光分解してスルホン酸を発生する化合物、特開昭61-166544号等に記載のジスルホン化合物を挙げることができる。

【0068】また、これらの光により酸を発生する基、あるいは化合物をポリマーの主鎖または側鎖に導入した化合物、たとえば、M. E. Woodhouse et al., J. Am. Chem. Soc., 104, 5586(1982)、S. P. Pappas et al., J. Imaging Sci., 30(5), 218(1986)、S. Kondo et al., Makromol. Chem., Rapid Commun., 9, 625(1988)、Y. Yamada et al., Makromol. Chem., 152, 153, 163(1972)、J. V. Crivello et al., J. Polym. Sci., Polymer Chem. Ed., 17, 3845(1979)、米国特許第3,849,137号、獨国特許第3914407号、特開昭63-26653号、特開昭55-164824号、特開昭62-69263号、特開昭63-146038号、特開昭63-163452号、特開昭62-153853号、特開昭63-146029号等に記載の化合物を用いることができる。

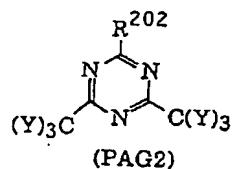
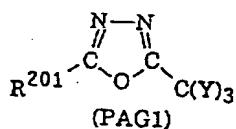
【0069】さらにV. N. R. Pillai, Synthesis, (1), 1(1980)、A. Abad et al., Tetrahedron Lett., (47) 4555(1971)、D. H. R. Barton et al., J. Chem. Soc., (C), 329(1970)、米国特許第3,779,778号、欧州特許第126,712号等に記載の光により酸を発生する化合物も使用することができる。

【0070】上記併用可能な活性光線または放射線の照射により分解して酸を発生する化合物の中で、特に有効に用いられるものについて以下に説明する。

(1) トリハロメチル基が置換した下記一般式(PAG1)で表されるオキサゾール誘導体または一般式(PAG2)で表されるS-トリアジン誘導体。

【0071】

【化20】

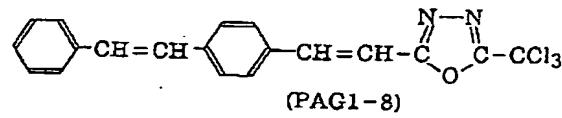
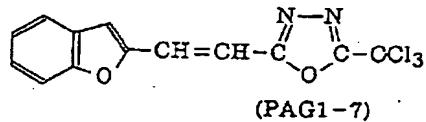
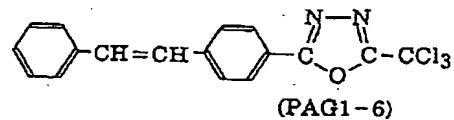
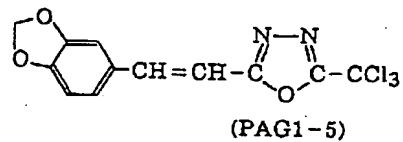
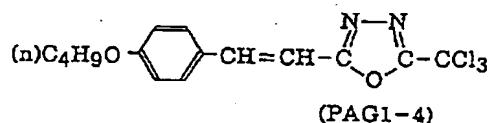
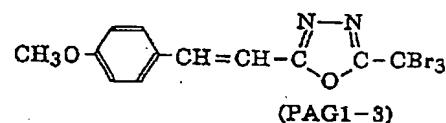
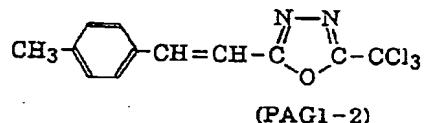
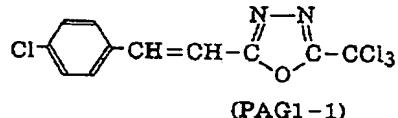


【0072】式中、R²⁰¹は置換もしくは未置換のアリール基、アルケニル基、R²⁰²は置換もしくは未置換のアリール基、アルケニル基、アルキル基、-C(Y)₃をしめす。Yは塩素原子または臭素原子を示す。具体的に

は以下の化合物を挙げることができるがこれらに限定されるものではない。

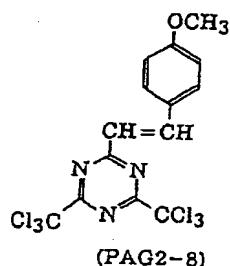
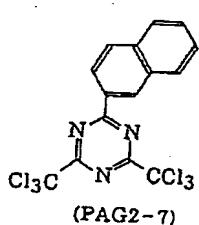
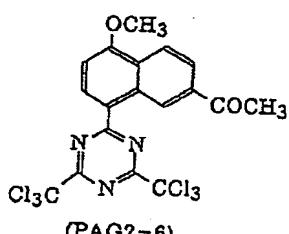
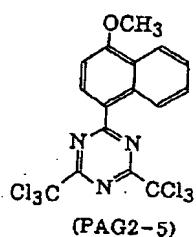
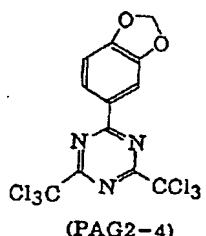
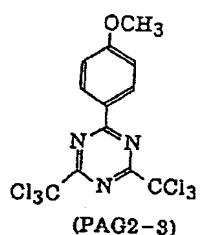
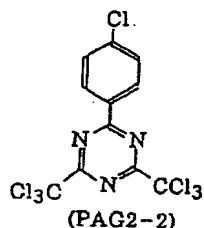
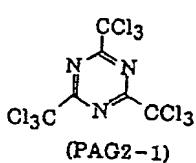
【0073】

【化21】

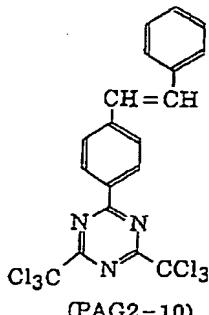
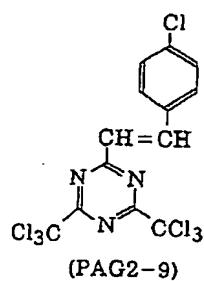


【0074】

【化22】

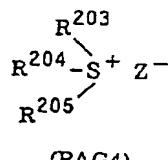
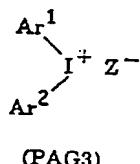


【0075】
【化23】



【0076】(2) 下記の一般式 (PAG3) で表されるヨードニウム塩、または一般式 (PAG4) で表されるスルホニウム塩。

【0077】
【化24】



【0078】式中、Ar¹、Ar²は各々独立に置換もしくは未置換のアリール基を示す。ここで、好ましい置換基としては、アルキル基、ハロアルキル基、シクロアルキル基、アリール基、アルコキシ基、ニトロ基、カルボキシル基、アルコキカルボニル基、ヒドロキシ基、メルカプト基およびハロゲン原子が挙げられる。

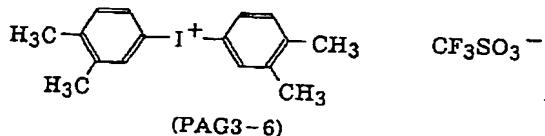
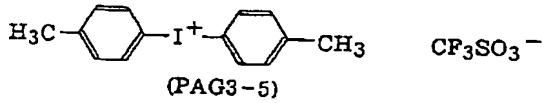
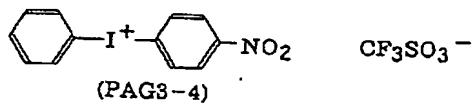
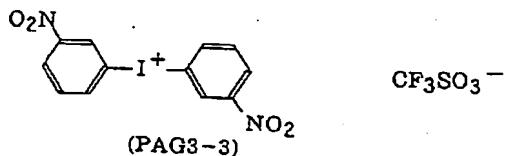
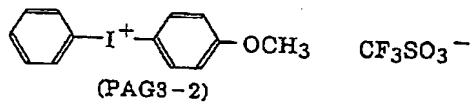
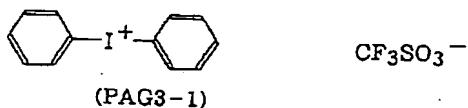
【0079】R²⁰³、R²⁰⁴、R²⁰⁵は各々独立に、置換もしくは未置換のアルキル基、アリール基を示す。好ましくは、炭素数6～14のアリール基、炭素数1～8のアルキル基およびそれらの置換誘導体である。好ましい置換基としては、アリール基に対しては炭素数1～8のアルコキシ基、炭素数1～8のアルキル基、ニトロ基、カルボキシル基、ヒドロキシ基およびハロゲン原子

であり、アルキル基に対しては炭素数1～8のアルコキシ基、カルボキシリ基、アルコキシカルボニル基である。

【0080】 Z^- は対アニオンを示し、 $CF_3SO_3^-$ 等のパーカルオロアルカンスルホン酸アニオン、ペンタフルオロベンゼンスルホン酸アニオンを示す。またR203、R204、R205のうちの2つおよびAr1、Ar2はそれぞれの単結合または置換基を介して結合してもよい。具体例としては以下に示す化合物が挙げられるが、これらに限定されるものではない。

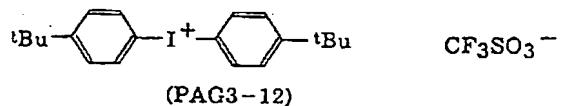
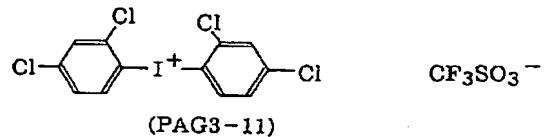
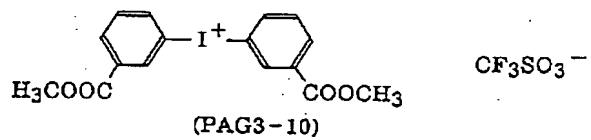
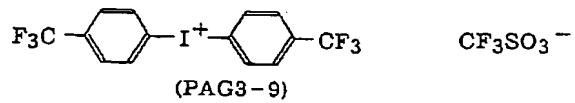
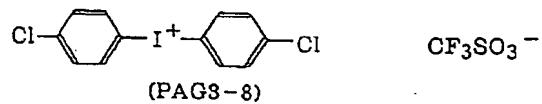
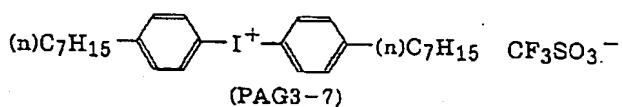
【0081】

【化25】

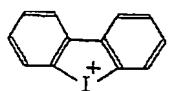


【0082】

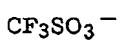
【化26】



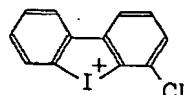
[0083]
[化27]



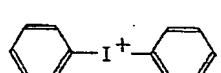
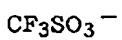
(PAG3-13)



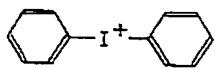
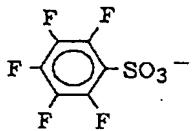
【0084】
【化28】



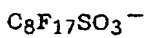
(PAG3-14)

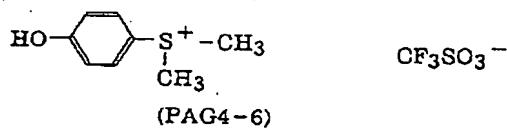
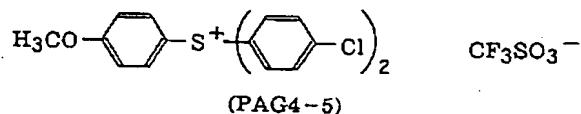
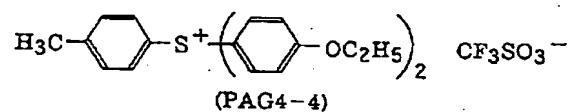
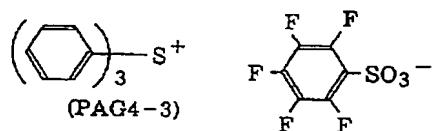
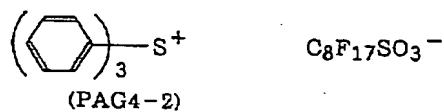
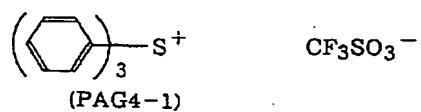


(PAG3-15)



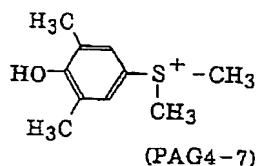
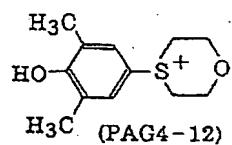
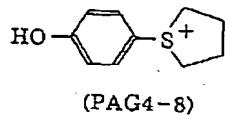
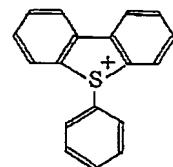
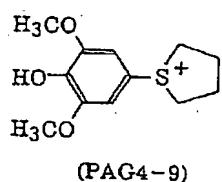
(PAG3-16)



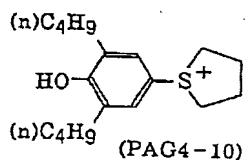
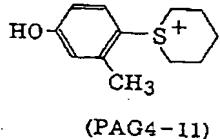
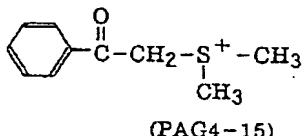


【0085】

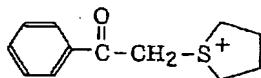
【化29】

 CF_3SO_3^-  CF_3SO_3^-  CF_3SO_3^-  CF_3SO_3^-  CF_3SO_3^-

(PAG4-13)

 CF_3SO_3^- $\text{C}_8\text{F}_{17}\text{SO}_3^-$  CF_3SO_3^- 

(PAG4-15)

 CF_3SO_3^- 

(PAG4-16)

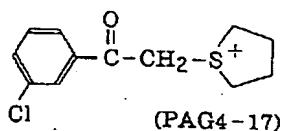
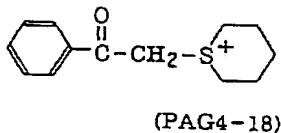
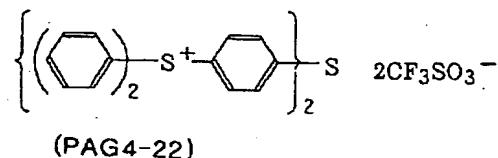
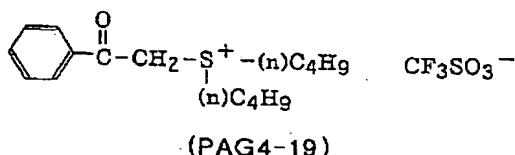
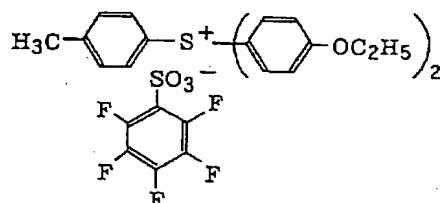
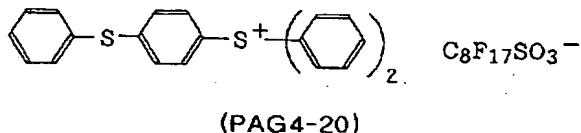
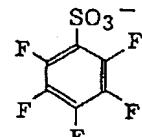
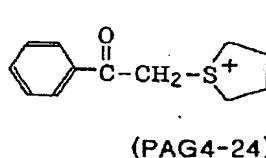
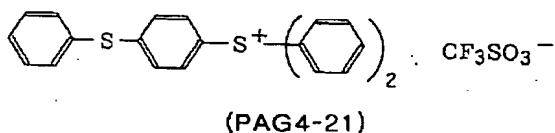
 CF_3SO_3^-

【0086】

【化30】

【0087】

【化31】

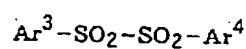
 CF_3SO_3^-  CF_3SO_3^-  CF_3SO_3^-  $\text{C}_8\text{F}_{17}\text{SO}_3^-$  CF_3SO_3^-

【0088】
【化32】

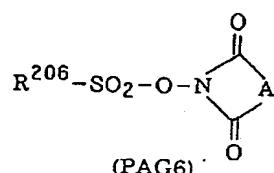
【0089】一般式 (PAG3)、(PAG4) で示される上記オニウム塩は公知であり、たとえば J. W. Knapczyk et al, J. Am. Chem. Soc., 91, 145 (1969)、A. L. Maycock et al, J. Org. Chem., 35, 2532, (1970)、E. Goethals et al, Bull. Soc. Chem. Belg., 73, 546, (1964)、H. M. Leicester, J. Amer. Chem. Soc., 51, 3587 (1929)、J. V. Crivello et al, J. Polym. Chem. Ed., 18, 2677 (1980)、米国特許第2,807,648号および同4,247,473号、特開昭53-101,331号等に記載の方法により合成することができる。

(3) 下記一般式 (PAG5) で表されるジスルホン誘導体または一般式 (PAG6) で表されるイミノスルホネート誘導体。

【0090】
【化33】

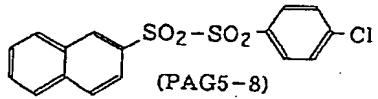
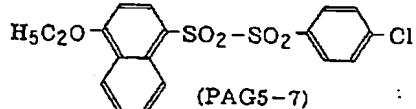
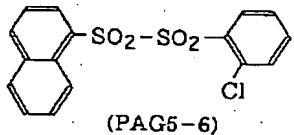
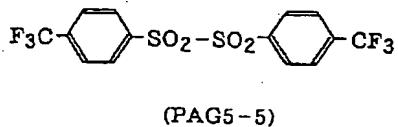
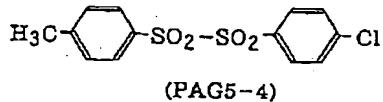
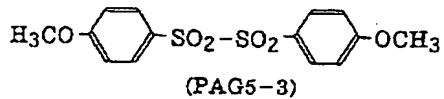
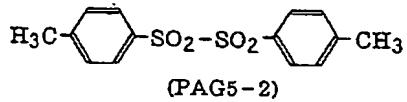
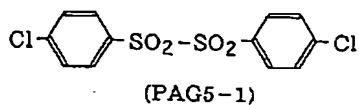


(PAG5)

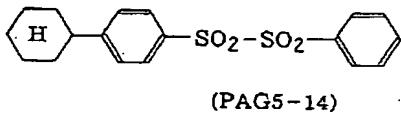
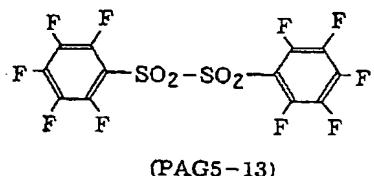
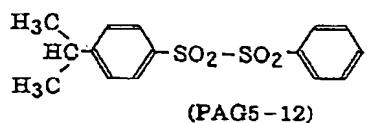
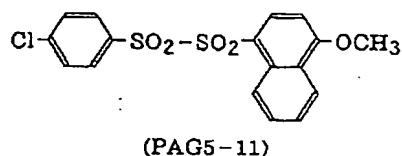
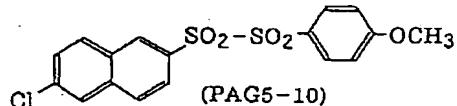
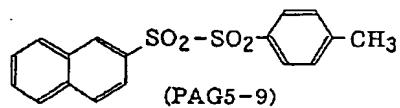


【0091】式中、 Ar^3 、 Ar^4 は各々独立に置換もしくは未置換のアリール基を示す。 R^{206} は置換もしくは未置換のアルキル基、アリール基を示す。A は置換もしくは未置換のアルキレン基、アルケニレン基、アリーレン基を示す。具体例としては以下に示す化合物が挙げられるが、これらに限定されるものではない。

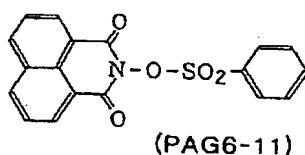
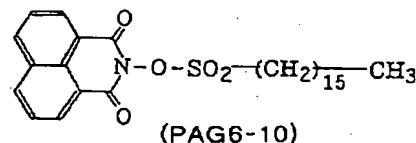
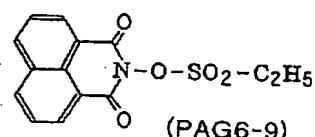
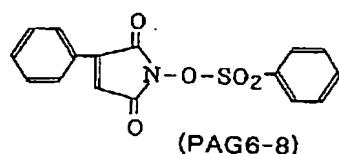
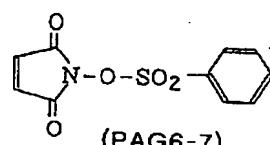
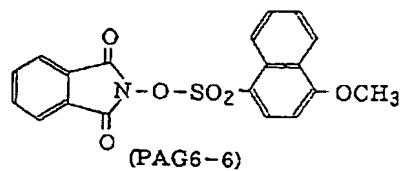
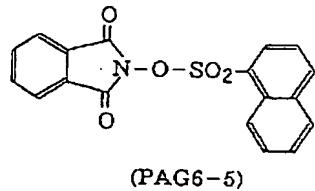
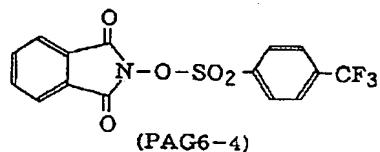
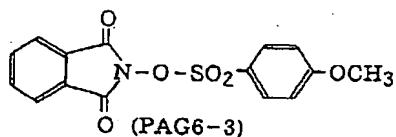
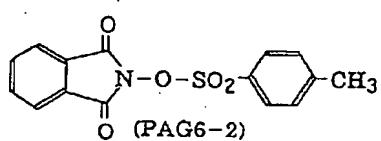
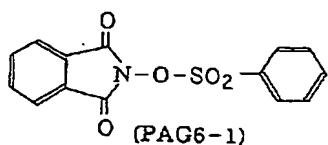
【0092】
【化34】



【0093】
【化35】

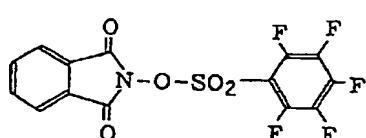
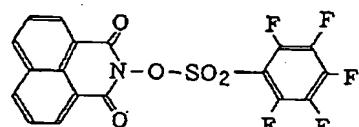
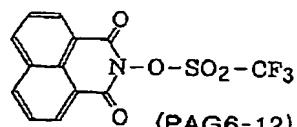


【0094】
【化36】



【0096】

【化38】



【0097】 ポジ型フォトレジスト組成物には系のアルカリ溶解性を向上させる目的や、系のガラス転移温度を

【0095】

【化37】

調節し、膜がもろくなったり、耐熱性が劣化したりすることを防ぐ目的で適當なアルカリ可溶性の低分子化合物を添加してもよい。このアルカリ可溶性低分子化合物としては、ジアルキルスルフォンアミド化合物やジアルキルスルフォニルイミド ($-SO_2-NH-CO-$) 化合物、ジアルキルジスルフォニルイミド ($-SO_2-NH-SO_2-$) 化合物などの分子内に酸性基を含有する化合物を挙げることができる。このアルカリ可溶性の低分子化合物の含有量は、上記バインダー樹脂に対して、40重量%以下が好ましく、より好ましくは30重量%以下であり、更に好ましくは25重量%以下である。

【0098】本発明に関する組成物は、特定の溶剤に溶解して用いるとよい。そのような溶剤として好ましいものは、各固形成分が充分に溶解し、かつその溶液がスピンドルコート法などの方法で均一な塗布膜が形成可能な有機溶媒であればいかなる溶媒でもよい。また、単独でも2種類以上を混合して用いても良い。具体的には、n-ブロピルアルコール、イソブロピルアルコール、n-ブチルアルコール、ターシャルーブチルアルコール、メチルセロソルブアセテート、エチルセロソルブアセテート、プロピレングリコールモノエチルエーテルアセテート、乳酸メチル、乳酸エチル、酢酸2-メトキシブチル、酢酸2-エトキシエチル、ビルビン酸メチル、ビルビン酸エチル、3-メトキシプロピオン酸メチル、3-メトキシプロピオン酸エチル、N-メチル-2-ピロリジノン、シクロヘキサン、シクロペントノン、シクロヘキサノール、メチルエチルケトン、1,4-ジオキサン、エチレングリコールモノメチルエーテル、エチレングリコールモノメチルエーテルアセテート、エチレングリコールモノエチルエーテル、エチレングリコールモノイソブロピルエーテル、ジエチレングリコールモノメチルエーテル、ジエチレングリコールジメチルエーテル、2-ヘプタノンなどが挙げられるが、もちろんこれらだけに限定されるものではない。

【0099】また本発明のポジ型フォトレジスト組成物には、更に必要に応じて界面活性剤、色素、安定剤、塗布性改良剤、染料などの他の成分を添加しても構わない。本発明のこのようなポジ型フォトレジスト組成物は基板上に塗布され、薄膜を形成する。この塗膜の膜厚は0.4~1.5μmが好ましい。露光手段としては、ArFエキシマレーザーステッパー露光など、露光波長が170~220nmの範囲に含まれるのが好ましく、

合成例(5) 樹脂Aの合成

トリシクロデカニルメタクリレート
単量体 [II-A-2]
メタクリル酸
THF

を溶解させた後、窒素を30分間吹き込み、反応液を65°Cに加熱した。重合開始剤としてV-65(和光純薬製)150mgを5回に分けて1時間おきに添加した。

特に好ましいのはArFエキシマレーザーステッパーである。

【0100】

【実施例】以下、本発明を実施例を示して具体的に説明するが、本発明の内容がこれらに限定されるものではない。

合成例(1) 単量体 [II-A-2] の合成

メタクリル酸86gをジクロロメタン500mLに溶解し、4-ジメチルアミノピリジン10g加えた。さらに、2-ヒドロキシ-γ-ブチロラクトン102gを静かに加えた。これを氷浴で冷却し、さらにジシクロヘキシカルボジイミド25gをゆっくりと加えた。そのまま30分攪拌した後、氷浴をはずし室温まで自然昇温し、室温下3時間攪拌した。反応終了後析出した粉体を濾別し、得られた濾液を10%塩酸水で抽出、さらに重曹水で洗浄後、飽和食塩水で洗い、得られた油層を濃縮した。これをシリカゲルカラムクロマトグラフィーを用いて精製し、目的の単量体 [II-A-2] 1.50gを得た。

【0101】合成例(2) 単量体 [II-C-2] の合成

合成例(1)のメタクリル酸を共栄社化学製ライトエステルHO-MSに代えた他は全く同様の操作で単量体 [II-C-2] を合成した。

【0102】合成例(3) 単量体 [II-F-2] の合成

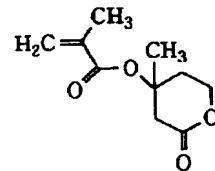
合成例(1)のメタクリル酸の代わりに、3-ヒドロキシプロピオン酸と昭和電工製カレンズMOIを反応させ合成した末端カルボン酸メタクリレートを用いた他は同様の方法で単量体 [II-F-2] を合成した。

【0103】合成例(4) 比較用単量体-1の合成

メバロニックラクトンとメタクリル酸クロリドにより、下記構造の単量体をJournal of Photopolymer Science and Technology Vol. 9, Number 3(1996) 509に記載の方に準じて合成した。

【0104】

【化39】



【0105】

22.0 g
13.6 g
1.7 g
87 g

最終の開始剤を添加した後、そのまま4時間加熱攪拌した。加熱終了後反応液を室温に戻し、THF 200gを添加し、反応液を希釈したものを蒸留水4L/メタノ

ール2Lの混合溶媒に再沈し、目的の樹脂Aを白色粉体として回収した。得られた共重合体のG P C分析を行つたところ、標準ポリスチレン換算にて重量平均分子量は

合成例(6) 樹脂Bの合成

トリシクロデカニルメタクリレート
単量体 [II-C-2]
メタクリル酸
THF

を溶解させた後、窒素を30分間吹き込み、反応液を65°Cに加熱した。重合開始剤としてV-65(和光純薬製)150mgを5回に分けて1時間おきに添加した。最終の開始剤を添加した後、そのまま4時間加熱攪拌した。加熱終了後反応液を室温に戻し、THF 200gを添加し、反応液を希釈したものを蒸留水4L/メタノ

合成例(7) 樹脂Cの合成

トリシクロデカニルメタクリレート
単量体 [II-F-2]
メタクリル酸
THF

を溶解させた後、窒素を30分間吹き込み、反応液を65°Cに加熱した。重合開始剤としてV-65(和光純薬製)150mgを5回に分けて1時間おきに添加した。最終の開始剤を添加した後、そのまま4時間加熱攪拌した。加熱終了後反応液を室温に戻し、THF 200gを添加し、反応液を希釈したものを蒸留水4L/メタノ

合成例(8) 樹脂Dの合成

トリシクロデカニルメタクリレート
単量体 [II-A-2]
t-ブチルメタクリレート
メタクリル酸
THF

を溶解させた後、窒素を30分間吹き込み、反応液を65°Cに加熱した。重合開始剤としてV-65(和光純薬製)150mgを5回に分けて1時間おきに添加した。最終の開始剤を添加した後、そのまま4時間加熱攪拌した。加熱終了後反応液を室温に戻し、THF 200gを添加し、反応液を希釈したものを蒸留水4L/メタノ

合成例(9) 樹脂Eの合成

トリシクロデカニルメタクリレート
単量体 [II-C-2]
t-ブチルメタクリレート
メタクリル酸
THF

を溶解させた後、窒素を30分間吹き込み、反応液を65°Cに加熱した。重合開始剤としてV-65(和光純薬製)150mgを5回に分けて1時間おきに添加した。最終の開始剤を添加した後、そのまま4時間加熱攪拌した。加熱終了後反応液を室温に戻し、THF 200gを添加し、反応液を希釈したものを蒸留水4L/メタノ

合成例(10) 樹脂Fの合成

36000であった。

【0106】

22.0 g
25.1 g
1.7 g
114 g

ール2Lの混合溶媒に再沈し、目的の樹脂Bを白色粉体として回収した。得られた共重合体のG P C分析を行つたところ、標準ポリスチレン換算にて重量平均分子量は37500であった。

【0107】

22.0 g
32.9 g
1.7 g
133 g

ール2Lの混合溶媒に再沈し、目的の樹脂Cを白色粉体として回収した。得られた共重合体のG P C分析を行つたところ、標準ポリスチレン換算にて重量平均分子量は39000であった。

【0108】

17.6 g
10.2 g
5.7 g
1.7 g
82 g

ール2Lの混合溶媒に再沈し、目的の樹脂Dを白色粉体として回収した。得られた共重合体のG P C分析を行つたところ、標準ポリスチレン換算にて重量平均分子量は35500であった。

【0109】

17.6 g
18.9 g
5.7 g
1.7 g
102 g

ール2Lの混合溶媒に再沈し、目的の樹脂Eを白色粉体として回収した。得られた共重合体のG P C分析を行つたところ、標準ポリスチレン換算にて重量平均分子量は37200であった。

【0110】

トリシクロデカニルメタクリレート	17.6 g
単量体 [II-F-2]	19.8 g
t-ブチルメタクリレート	5.7 g
メタクリル酸	1.7 g
THF	1.05 g

を溶解させた後、窒素を30分間吹き込み、反応液を65°Cに加熱した。重合開始剤としてV-65(和光純薬製)150mgを5回に分けて1時間おきに添加した。最終の開始剤を添加した後、そのまま4時間加熱攪拌した。加熱終了後反応液を室温に戻し、THF 200gを添加し、反応液を希釈したものを蒸留水4L/メタノール2Lの混合溶媒に再沈し、目的の樹脂Fを白色粉体として回収した。得られた共重合体のGPC分析を行ったところ、標準ポリスチレン換算にて重量平均分子量は38500であった。

【0111】

合成例 (11) 比較用樹脂Gの合成	
トリシクロデカニルメタクリレート	22.0 g
比較用単量体-1	19.9 g
メタクリル酸	1.7 g
THF	1.02 g

を溶解させた後、窒素を30分間吹き込み、反応液を65°Cに加熱した。重合開始剤としてV-65(和光純薬製)150mgを5回に分けて1時間おきに添加した。最終の開始剤を添加した後、そのまま4時間加熱攪拌した。加熱終了後反応液を室温に戻し、THF 200gを添加し、反応液を希釈したものを蒸留水4L/メタノール2Lの混合溶媒に再沈し、目的の樹脂Gを白色粉体として回収した。得られた共重合体のGPC分析を行ったところ、標準ポリスチレン換算にて重量平均分子量は35600であった。

【0112】

合成例 (12) 比較用樹脂Hの合成	
トリシクロデカニルメタクリレート	17.6 g
比較用単量体-1	12.0 g
t-ブチルメタクリレート	5.7 g
メタクリル酸	1.7 g
THF	8.6 g

を溶解させた後、窒素を30分間吹き込み、反応液を65°Cに加熱した。重合開始剤としてV-65(和光純薬製)150mgを5回に分けて1時間おきに添加した。最終の開始剤を添加した後、そのまま4時間加熱攪拌した。加熱終了後反応液を室温に戻し、THF 200gを添加し、反応液を希釈したものを蒸留水4L/メタノール2Lの混合溶媒に再沈し、目的の樹脂Hを白色粉体として回収した。得られた共重合体のGPC分析を行ったところ、標準ポリスチレン換算にて重量平均分子量は34500であった。

【0113】合成例 (13)

光酸発生剤(1)を合成した。水酸化ナトリウム8gとヒドロキシアミン塩酸塩14gとを蒸留水200ミリリットルに溶解し、ジメチルマレイン酸無水物25gを加えた後、室温で5時間攪拌し、続けて100°Cで3時間加熱攪拌した。反応終了後、反応液に塩酸水を加え、更に塩化ナトリウムで飽和させた後、酢酸エチルで抽出した。抽出した酢酸エチル溶液を1/3に濃縮、トルエンを加え、再度濃縮する操作を繰り返し、N-ヒドロキシマレインイミド体15gを単離した。

【0114】このようにして合成したN-ヒドロキシマレインイミド体4.2gをジクロロメタンに溶解し、氷

トリシクロデカニルメタクリレート	17.6 g
比較用単量体-1	19.8 g
t-ブチルメタクリレート	5.7 g
メタクリル酸	1.7 g
THF	1.05 g

を溶解させた後、窒素を30分間吹き込み、反応液を65°Cに加熱した。重合開始剤としてV-65(和光純薬製)150mgを5回に分けて1時間おきに添加した。最終の開始剤を添加した後、そのまま4時間加熱攪拌した。加熱終了後反応液を室温に戻し、THF 200gを添加し、反応液を希釈したものを蒸留水4L/メタノ

トリシクロデカニルメタクリレート	22.0 g
比較用単量体-1	19.9 g
メタクリル酸	1.7 g
THF	1.02 g

を溶解させた後、窒素を30分間吹き込み、反応液を65°Cに加熱した。重合開始剤としてV-65(和光純薬製)150mgを5回に分けて1時間おきに添加した。最終の開始剤を添加した後、そのまま4時間加熱攪拌した。加熱終了後反応液を室温に戻し、THF 200gを添加し、反応液を希釈したものを蒸留水4L/メタノール2Lの混合溶媒に再沈し、目的の樹脂Gを白色粉体として回収した。得られた共重合体のGPC分析を行ったところ、標準ポリスチレン換算にて重量平均分子量は35600であった。

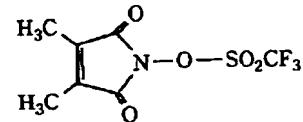
【0112】

合成例 (12) 比較用樹脂Hの合成	
トリシクロデカニルメタクリレート	17.6 g
比較用単量体-1	12.0 g
t-ブチルメタクリレート	5.7 g
メタクリル酸	1.7 g
THF	8.6 g

を溶解させた後、窒素を30分間吹き込み、反応液を65°Cに加熱した。重合開始剤としてV-65(和光純薬製)150mgを5回に分けて1時間おきに添加した。最終の開始剤を添加した後、そのまま4時間加熱攪拌した。加熱終了後反応液を室温に戻し、THF 200gを添加し、反応液を希釈したものを蒸留水4L/メタノール2Lの混合溶媒に再沈し、目的の樹脂Hを白色粉体として回収した。得られた共重合体のGPC分析を行ったところ、標準ポリスチレン換算にて重量平均分子量は34500であった。

【0115】

【化40】



【0116】【実施例・比較例】上記合成例で合成した樹脂A～Hそれぞれ1.2gと、光酸発生剤(1)0.25gとを固体分14重量%の割合で2-ヘプタノンに溶解した後、0.1μmのミクロフィルターで濾過、ポジ型フォトレジスト組成物溶液を調製した。その処方を下記表1に示す。

【0117】(評価試験)得られたポジ型フォトレジスト組成物溶液をスピンドルコータを利用してシリコンウェハ

一上に塗布し、120°Cで90秒間乾燥、約0.5 μmのポジ型フォトレジスト膜を作成し、それにArFエキシマレーザー(193 nm)で露光した。露光後の加熱処理を110°Cで90秒間で行い、2.38%のテトラメチルアンモニウムヒドロキシド水溶液で現像、蒸留水でリーンし、レジストパターンプロファイルを得た。

【0118】〔相対感度〕：0.5 μmのパターンを再現できる露光量を感度とし、実施例1のレジスト感度を1とし、実施例1以外のレジストの相対感度を次式により求めた。すなわち

実施例1以外の感度／実施例1の感度

【0119】〔パターンプロファイル〕：上記で得られ

たレジストパターンプロファイルを走査型電子顕微鏡で観察し、矩形なものを○、T-トップ形状を示したものを作成して評価した。

【0120】〔密着性〕（残存細線の最小線幅）：上記で得られたレジストパターンプロファイルを走査型電子顕微鏡で観察し、残存している最も細線の線幅をもって評価した。即ち、密着性がより高いものは、より細かい線幅のパターンも残存するが、逆に密着性の劣るものは細かい線幅ほど基板界面で密着できず、パターンが剥がれてしまう。結果を表1に示す。

【0121】

【表1】

表1

No	使用した樹脂	相対感度	パターンプロファイル	残存細線の最小線幅
実施例1	A	1.0	○	0.29
実施例2	B	0.9	○	0.30
実施例3	C	0.9	○	0.31
実施例4	D	0.6	○	0.28
実施例5	E	0.5	○	0.29
実施例6	F	0.6	○	0.30
比較例1	G	2.4	×	0.59
比較例2	H	1.7	×	0.60

【0122】比較例はいずれも、相対感度、パターンプロファイル、密着性の点で問題を含む。一方、本発明のポジ型フォトレジスト組成物に関する実施例1～6はそのすべてについて満足がいくレベルにある。すなわち、ArFエキシマレーザー露光を始めとする遠紫外線を用いたリソグラフィーに好適である。

【0123】

【発明の効果】以上説明したように本発明は、特に170 nm～220 nmという波長領域の光に対して十分好適であり、かつ高感度で、密着性に優れ、良好なレジストパターンプロファイルが得られるポジ型フォトレジスト組成物を提供できる。

* NOTICES *

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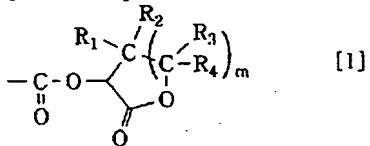
- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The positive type photoresist constituent characterized by containing the resin which has in intramolecular the ester group expressed with the following general formula [I], and disassembles according to an operation of an acid, and the solubility over an alkali solution increases, and the compound which generates an acid by the exposure of an activity beam of light or a radiation.

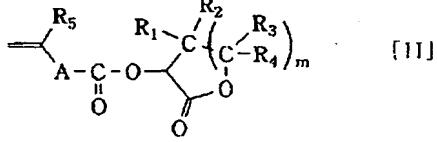
[Formula 1]



among a formula, R1 -R4 may be the same, or it may differ, and expresses a hydrogen atom or an alkyl group. m expresses 1 or 2.

[Claim 2] The positive type photoresist constituent according to claim 1 characterized by being resin which disassembles according to an operation of an acid and the solubility over an alkali solution increases, including the repeat structural unit by which said resin is equivalent to the monomer shown by the following general formula [II].

[Formula 2]



(R1 -R4 and m are synonymous with a thing according to claim 1 among a formula.) R5 A hydrogen atom or a methyl group is expressed. A expresses the radical which combined these [one radical chosen from single bond, an alkylene group, a permutation alkylene group, a ether group, a thioether radical, a carbonyl group, an ester group, an amide group, a sulfonamide radical a urethane group, and an urea radical, or] two or more.

[Claim 3] The positive type photoresist constituent according to claim 1 or 2 characterized by said resin including the repeat structural unit which has an aliphatic-cyclic-hydrocarbon part further.

[Claim 4] The positive type photoresist constituent according to claim 1 to 3 characterized by said resin including the repeat structural unit which has the radical which an operation of an acid decomposes [radical] further and increases the solubility in the inside of an alkali developer.

[Translation done.]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the positive type photoresist constituent with which the pattern in which the resist pattern which is high sensitivity in detail and was excellent about the suitable positive type photoresist constituent was obtained when [which it says is 170nm - 220nm also an activity beam of light or a radiation, and in it] exposure processing was carried out with light with short wavelength very much, and the adhesion with a substrate was excellent is obtained.

[0002]

[Description of the Prior Art] In recent years, in the field of the various electron device manufactures which need micro processing, such as a semiconductor device, the demand about the more and more densification of a device and high integration is increasing. The military requirement to the photography technique for realizing detailedization of a pattern in connection with this has reached to an extreme of severity. bearing a wing of this detailedized technique -- a photoresist -- high -- resolution --izing -- it is -- moreover, exposure light -- short wavelength -- it is--izing.

[0003] Generally, the resolution (Res) of optical system can be expressed, Rayleigh's formula (for a process factor and lambda, the wavelength of the exposure light source and NA are [k] numerical aperture of a lens), i.e., $Res = k \cdot \lambda / NA$. in order to make reappearance line breadth small, to resolve a detailed pattern from this formula, and to acquire high resolution namely,, it turns out that what is necessary is just to shorten wavelength at the time of exposure. To be sure, exposure wavelength shifts to g line (436nm) of a high pressure mercury vapor lamp, and i line (365nm) with contraction of the minimum reappearance line breadth, and the device manufacture which used the KrF excimer laser (248nm) further is considered. And to the further micro processing, promising ** of the use of ArF (193nm) is carried out also in the short wave excimer laser.

[0004] If an eye is moved to the direction of the photoresist exposed by short wave Nagamitsu, high integration by the multilayer-resist system more than not the monolayer resist that has led to manufacture--ization conventionally but two-layer [using surface lithography] is also considered. However, complicated--ization of the process which has so far obstructed utilization of a multilayer resist is still a problem. Moreover, primarily, that a gas life is short in the case of excimer lasers including a KrF excimer laser, and since the aligner itself is expensive, if it is necessary to raise the cost performance of laser, it is made general.

[0005] It is the so-called chemistry magnification mold resist to which having replied to this became in use from the KrF excimer laser exposure application. A chemistry magnification mold resist is the structure of an acid being generated from the photo-oxide generating agent which recognizes the amount existence of catalysts in a system by exposure, desorbing the protective group of a binder or the alkali fusibility radical of a low molecular weight compound in catalytic reaction with the acid of the amount of catalysts, and securing the soluble discrimination to an alkali developer. Since a chemistry magnification mold resist uses the acid generated by the photoreaction in catalytic reaction, it can expect high sensitivity--ization.

[0006] Generally a chemistry multiplier system resist can be divided roughly into three kinds, the common-name two-component system, a 2.5 component system, and 3 component system. The two-component system has combined a photo-oxide generating agent and binder resin. This binder resin is resin which has in intramolecular the radical (it is also called an acidolysis nature machine) which an operation of an acid decomposes [radical] and increases the solubility in the inside of the alkali developer of resin. A 2.5 component system contains the low molecular weight compound which has an acidolysis nature machine further in such the two-component system. 3 component system contains a photo-oxide generating agent, alkali fusibility resin, and the above-mentioned low molecular weight compound.

[0007] However, when exposure light became short wavelength, a new problem arose. That is, in a photoresist, the material with sufficient transparency has trouble in dry etching resistance to light with short wavelength. The material with sufficient dry etching resistance is the trouble that transparency is bad. Coexistence of dry etching resistance and transparency is the performance issue of the binder resin in a photoresist layer fundamentally. There are novolak resin and Pori p-hydroxystyrene as a binder. Novolak resin has use large as alkali fusibility resin for i line resists, and Pori p-hydroxystyrene has use as a base polymer for KrF excimer laser resists. These do not become a big problem as long as light with long wavelength is used. In the case of light with short wavelength, it differs. In the wavelength field of 170nm - 220nm, it has high optical density, and especially the above-mentioned resin cannot use these as a matter of fact directly as usual. For this reason, it has optical high transparency and looked forward to development of resin also with high dry etching resistance.

[0008] There is a method of introducing for example, an aliphatic-cyclic-hydrocarbon part into resin in one of the general replies to this problem. Moreover, there is also a method of using the 1 naphthalene frame of an aromatic compound. There are many examples of a report about filling the request of both which are called optical

transparency and dry etching resistance by installation of an aliphatic-cyclic-hydrocarbon part especially. For example, there are Journal of Photopolymer Science and technology vol.3, p439, 1992., etc.
 [0009] It passes further, the Tokiyasu quality is also influenced and it is [sensibility and resolution resolution and] especially important what on the other hand, is chosen as an acidolysis nature machine in the resin containing an acidolysis nature machine. [of a resist] Until now, as an acidolysis nature machine which protects carboxylic-acid radicals, acetal ester, such as the 3rd class alkyl ester, such as t-butyl ester, and tetrahydropyranyl ester, ethoxyethyl ester, is mainly reported. However, t-butyl ester group has the difficulty that the desorption capacity by the generated acid is low, and ** and sensibility will fall. Conversely, it was easy to decompose also in ordinary temperature, and tetrahydropyranyl ester, ethoxyethyl ester, etc. were holding the big problem in stability with the passage of time. Moreover, although JP,5-346668,A was performing the proposal which uses a 3-oxocyclohexyl ester group as an acidolysis nature machine, it was not necessarily a satisfying object in respect of sensibility. Thus, it was not necessarily clear in how the acidolysis nature machine which protected the carboxylic acids which are satisfied with coincidence of sensibility and preservation stability with the passage of time in a photoresist should be designed. Moreover, in the resist pattern obtained, in order to make reappearance line breadth small and to resolve a detailed pattern, sufficient adhesion to the substrate of not only the above-mentioned property but the obtained detailed pattern is needed. When this adhesion is insufficient, even if a detailed pattern is obtained, it may separate.

[0010]
 [Problem(s) to be Solved by the Invention] Therefore, to the light of the wavelength field of 170nm ~ 220nm, especially the purpose of this invention is suitable enough, and is to offer the positive type photoresist constituent in which the resist pattern profile which is high sensitivity and is obtained to light was excellent in, and the adhesion with a substrate was excellent.

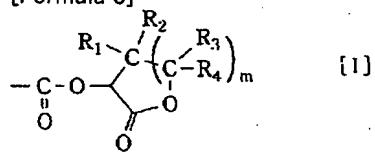
[0011]

[Means for Solving the Problem] As a result of inquiring wholeheartedly with careful attention to many above-mentioned properties, by using the resin which has the radical which has specific structure, this invention persons found out that the above-mentioned purpose was solved splendidly, and resulted in this invention. That is, the following configuration can attain the above-mentioned purpose.

(1) The positive type photoresist constituent characterized by containing the resin which has in intramolecular the ester group expressed with the following general formula [I], and disassembles according to an operation of an acid, and the solubility over an alkali solution increases, and the compound which generates an acid by the exposure of an activity beam of light or a radiation.

[0012]

[Formula 3]

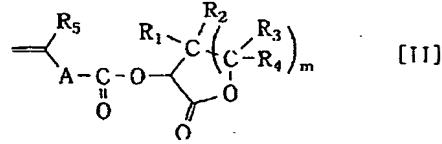


[0013] among a formula, R1 ~ R4 may be the same, or it may differ, and expresses a hydrogen atom or an alkyl group. m expresses 1 or 2.

(2) A positive type photoresist constituent given in the above (1) characterized by being resin which disassembles according to an operation of an acid and the solubility over an alkali solution increases, including the repeat structural unit by which said resin is equivalent to the monomer shown by the following general formula [II].

[0014]

[Formula 4]



[0015] (R1 ~ R4 and m are synonymous with a thing given in the above (1) among a formula.) R5 A hydrogen atom or a methyl group is expressed. A expresses the radical which combined these [one radical chosen from single bond, an alkylene group, a permutation alkylene group, a ether group, a thioether radical, a carbonyl group, an ester group, an amide group, a sulfonamide radical, a urethane group, and an urea radical, or] two or more.

(3) The above (1) characterized by said resin including the repeat structural unit which has an aliphatic-cyclic-hydrocarbon part further, or a positive type photoresist constituent given in (2).

(4) A positive type photoresist constituent given in either of aforementioned (1) ~ (3) characterized by said resin including the repeat structural unit which has the radical which an operation of an acid decomposes [radical] further and increases the solubility in the inside of an alkali developer.

[0016]

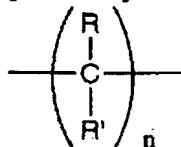
[Embodiment of the Invention] Hereafter, this invention is explained to a detail. R1 ~ R4 in a general formula [I] As a shown alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, an isobutyl radical, and sec-butyl, are desirable, are a methyl group, an ethyl group, a propyl group, an isopropyl group, and butyl more preferably, and are a methyl group and an ethyl group still more preferably. m expresses 1 or 2 and is 1 preferably.

[0017] As parent resin in the resin containing the radical shown by the above-mentioned general formula [I], as long as the effectiveness of this invention is acquired, which thing may be used. In this invention, resin including the

repeat structural unit which is equivalent to the monomer shown by the above-mentioned general formula [II] as resin containing the radical shown by the general formula [I] is desirable. This resin can be obtained by carrying out the radical polymerization of the monomer shown for example, by the above-mentioned general formula [II].
 [0018] As A in the above-mentioned general formula [II], they are one radical chosen from single bond or an alkylene group, a permutation alkylene group, a ether group, a thioether radical, a carbonyl group, an ester group, the amide group, the sulfane amide group, the urethane group, and the urea radical, or the radical combined two or more. The radical shown below can be mentioned as the alkylene group of A, and a permutation alkylene group.

[0019]

[Formula 5]

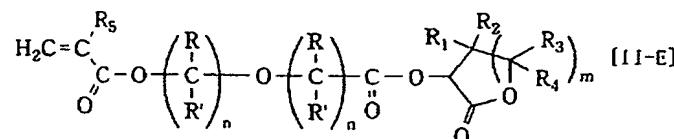
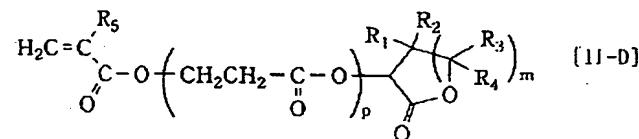
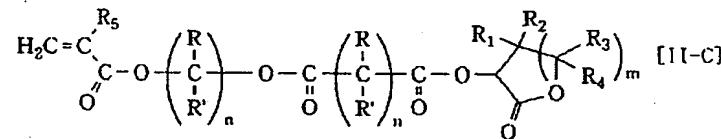
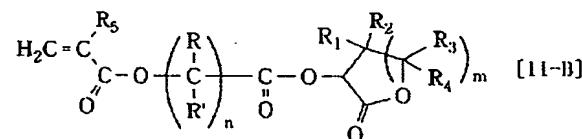
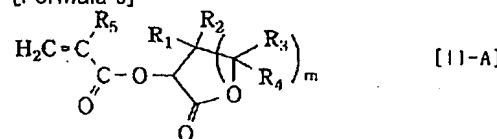


[0020] R, R': A hydrogen atom, an alkyl group, a permutation alkyl group, a halogen atom, a hydroxyl group, or an alkoxy group is expressed, and even if both are the same, they may differ. As an alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, and butyl, are a methyl group, an ethyl group, a propyl group, or an isopropyl group desirable still more preferably here. As a substituent of a permutation alkyl group, a hydroxyl group, a halogen atom, and an alkoxy group can be mentioned. As an alkoxy group, the thing of 1-4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned. n expresses the integer of 1-10.

[0021] One radical chosen also in the above as A from single bond or an alkylene group, a permutation alkylene group, a ether group, the amide group, the urethane group, and the urea radical or especially the radical combined two or more is desirable. Here, as an alkylene group and a permutation alkylene group, the alkylene group of 1-4 carbon numbers is desirable, and a methylene group, ethylene, a propylene radical, a butylene radical, a methylation methylene group, a dimethyl permutation methylene group, methylation ethylene, dimethyl permutation ethylene, a methylation propylene radical, and a dimethyl permutation propylene radical are specifically mentioned. The monomer expressed with general formula [II-A] - [II-E] as a desirable thing below among the monomers shown by the general formula [II] can be mentioned.

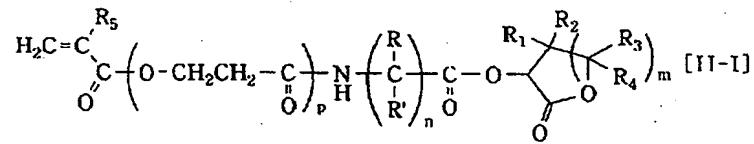
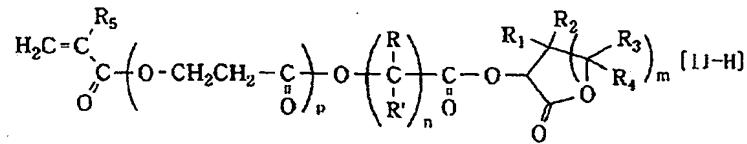
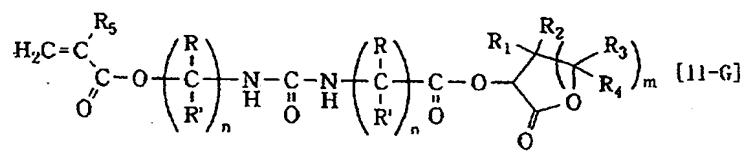
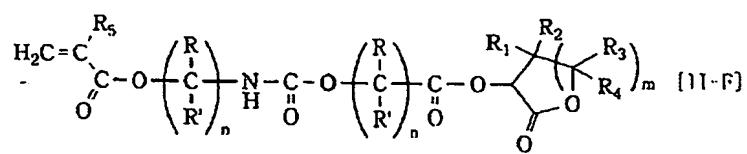
[0022]

[Formula 6]



[0023]

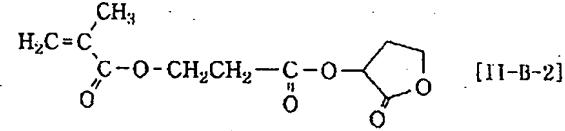
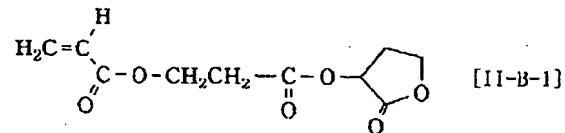
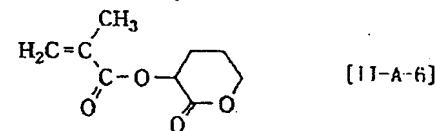
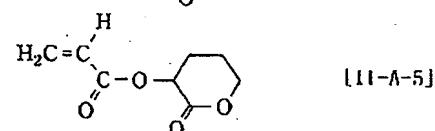
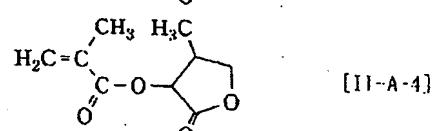
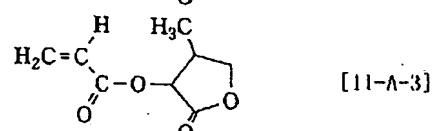
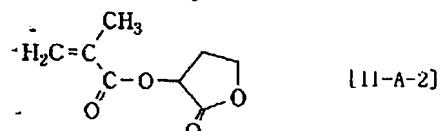
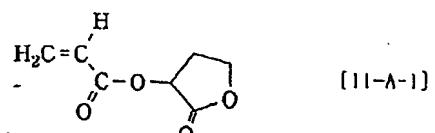
[Formula 7]



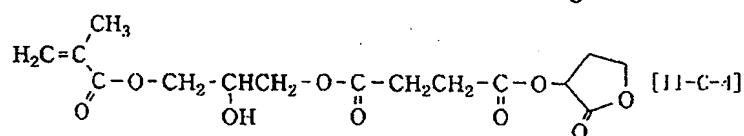
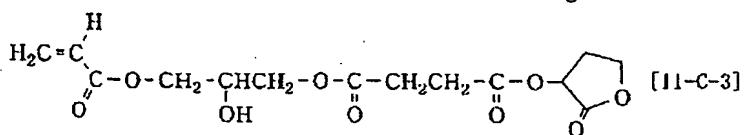
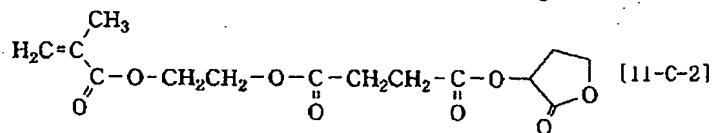
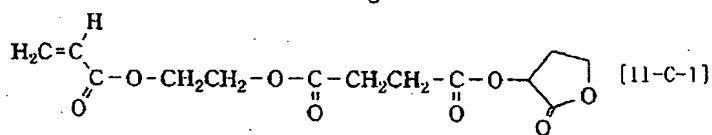
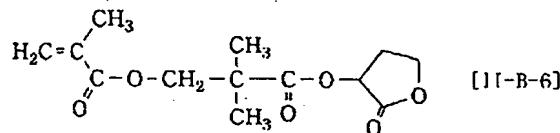
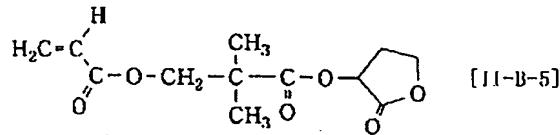
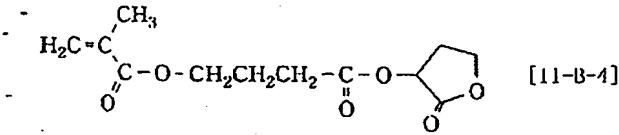
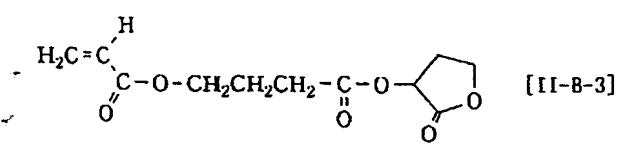
[0024] In the above-mentioned general formula, R1-R5, R, R', and n and m are respectively synonymous with the above. p expresses the number of 1-3. The example of the monomer shown by the general formula [II] below is shown. However, these do not limit the contents of this invention.

[0025]

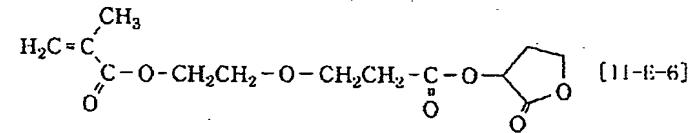
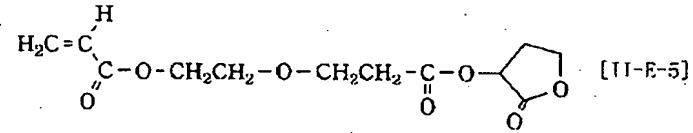
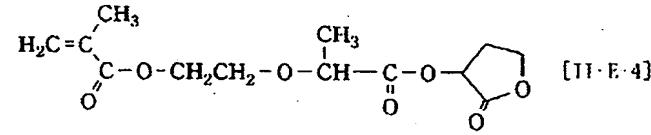
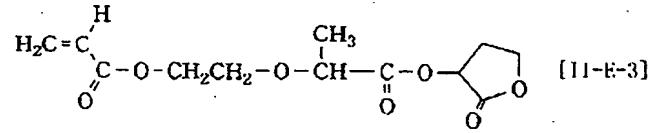
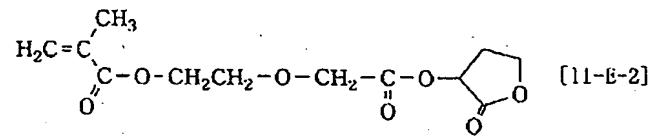
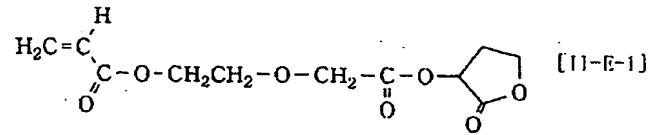
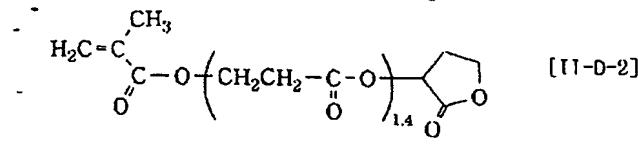
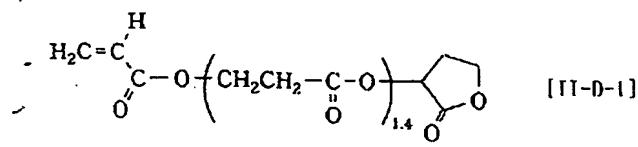
[Formula 8]



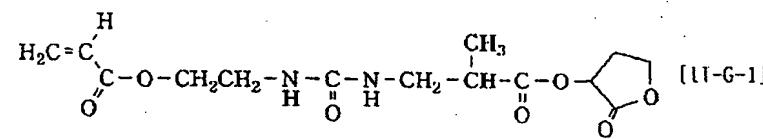
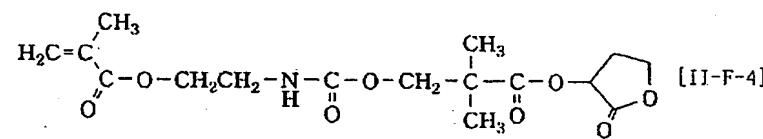
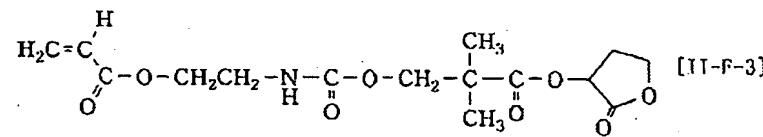
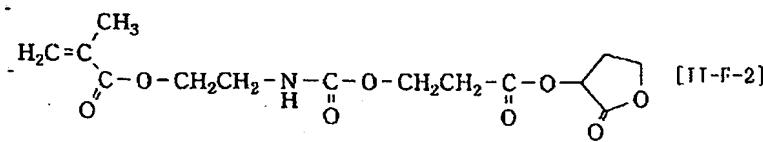
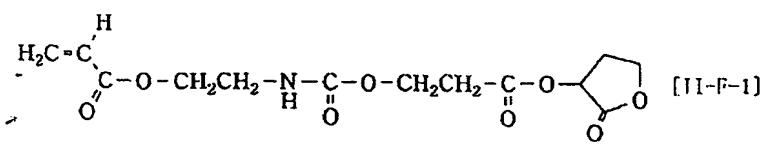
[0026]
[Formula 9]



[0027]
[Formula 10]

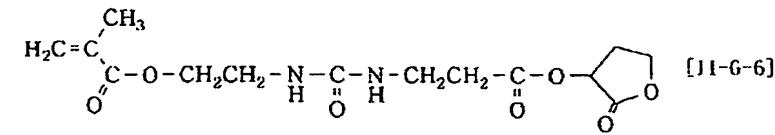
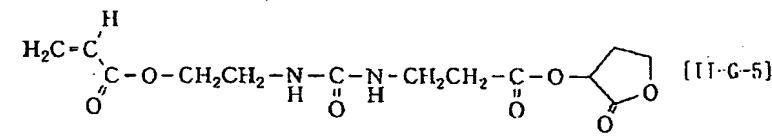
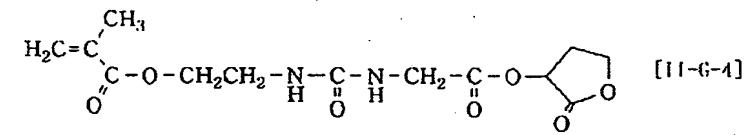
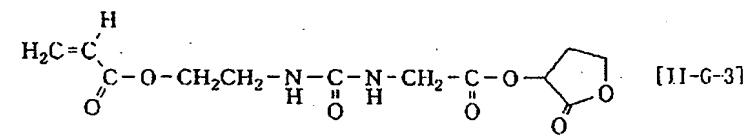
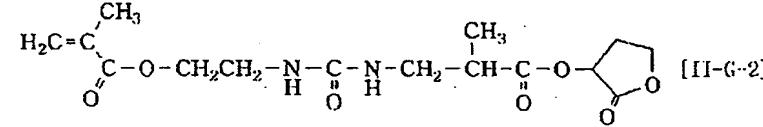


[0028]
[Formula 11]



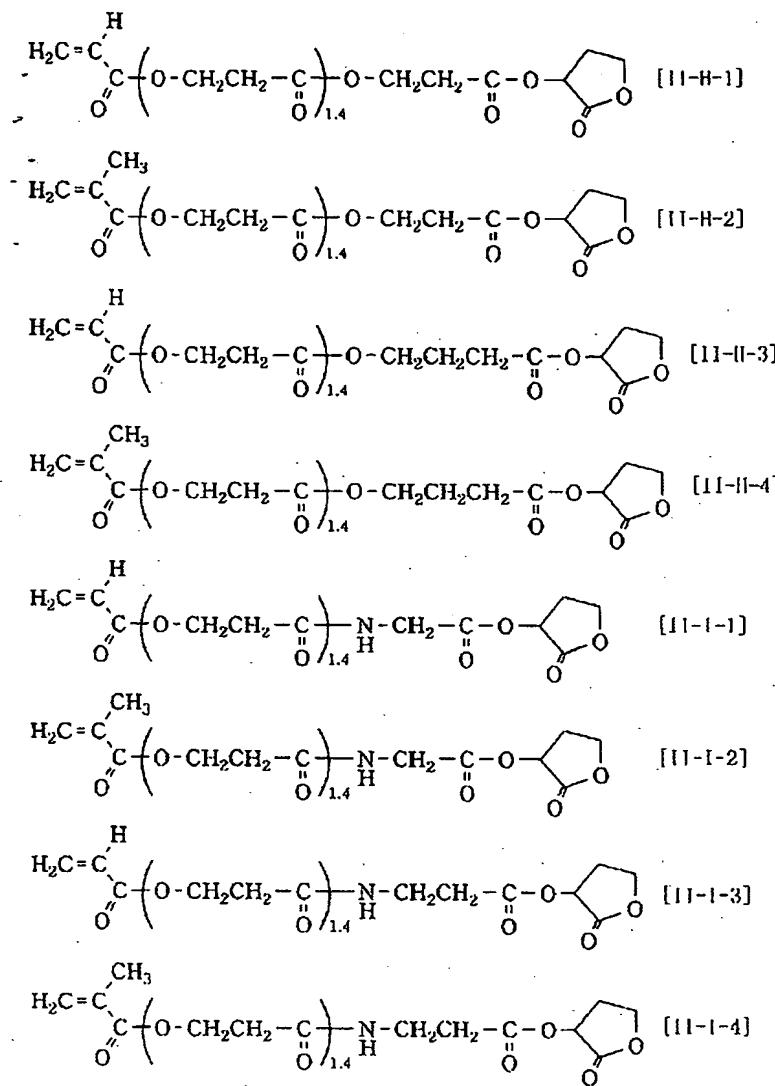
[0029]

[Formula 12]



[0030]

[Formula 13]

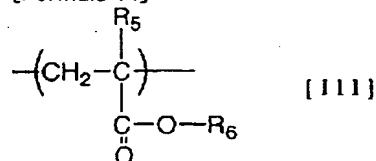


[0031] The monomer shown by such general formula [II] is the carboxylic acids and 2-hydroxy lactone which have in intramolecular the carbon-carbon double bond in which a radical polymerization is possible Ansgew.Chem.int.Ed.Engl., 1978, 17, and 522 It is compoundable by making the carboxylic-acid chloride and 2-hydroxy lactone which esterify or correspond by the approach of a publication react under a basic condition.

[0032] As for the resin in the positive type photoresist constituent of this invention, it is desirable to include the repeat structural unit which has an aliphatic-cyclic-hydrocarbon part in intramolecular with the radical shown by the above-mentioned general formula [I]. Thereby, the dry etching resistance of a positive type photoresist can be raised. As a repeat structural unit which has an aliphatic-cyclic-hydrocarbon part in intramolecular, it is the following general formula [III], for example. Or the repeat structural unit shown by [IV] can be mentioned.

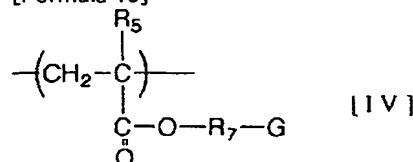
[0033]

[Formula 14]



[0034]

[Formula 15]

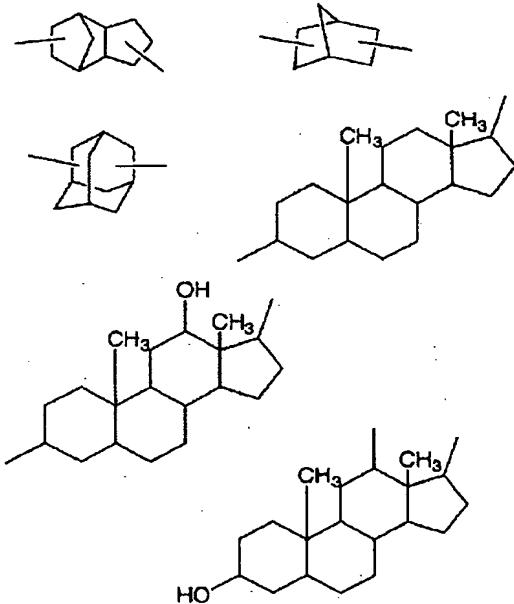


[0035] General formula [III] Inner R6 It is a univalent aliphatic-cyclic-hydrocarbon radical. Specifically, an

adamantyl radical, a 2-methyl-2-adamanthyl radical, a norbornyl radical, a BORONIRU radical, an isoboronyl radical, a tricyclo deca nyl radical, a JISHIKURO pentenyl radical, the Novo Renan epoxy group, a menthyl radical, an iso-menthyl radical, a neomenthyl radical, etc. can be mentioned. The inside of a general formula [IV], and R7 It is the connection radical which has a divalent aliphatic-cyclic-hydrocarbon part. G is -COOH, -OH, and -COOR8. Or -OR8 It expresses. R8 The 3rd class alkyl group, a tetrahydropyranyl group, a tetrahydrofuranyl radical, -CH₂ OR9, or -CH(CH₃) OR9 It expresses. R9 An alkyl group is expressed. R5 It is synonymous with the above. R7 As an aliphatic-cyclic-hydrocarbon part included in a connection radical, the following structures can be mentioned, for example.

-[0036]

[Formula 16]



[0037] Moreover, R7 which connects G sets with the above-mentioned aliphatic-cyclic-hydrocarbon part, an ester group, or the above-mentioned aliphatic-cyclic-hydrocarbon part As an inner connection radical, single bond is sufficient, and the radical which combined one radical chosen from an alkylene group, a ether group, a thioether radical, a carbonyl group, an ester group, an amide group, a sulfonamide radical, etc. or two or more can be mentioned.

[0038] - COOR8 A radical or -OR8 R8 in a radical The 3rd class alkyl groups, such as t-butyl and t-ethyl group, a tetrahydropyranyl group, A tetrahydrofuranyl radical and -CH(CH₃) OCH₂ CH₃ Radical, -CH(CH₃) OCH₂ CH₂ (CH₃) 1-alkoxy ethyl groups, such as a radical, and -CH₂ OCH₃ A radical and -CH₂ OCH₂ CH₃ The substituent decomposed according to an operation of acids, such as alkoxy methyl groups, such as a radical, is expressed.

[0039] Among the above-mentioned resin, three-mol % - 60-mol% of the content of the repeat structural unit containing the radical shown by the general formula [I] is desirable to all repeat units, and is five-mol % - 50-mol % more preferably. In the case of below 3 mol %; the effectiveness of this invention is hard to be discovered and is not desirable. If 60-mol % is exceeded, dry etching resistance becomes easy to deteriorate and is not desirable. 97-40-mol% of the content in the resin of the repeat structural unit which has an aliphatic-cyclic-hydrocarbon part in intramolecular is desirable to all repeat units, and is 95-50-mol % more preferably.

[0040] As for the resin concerning above-mentioned this invention, it is desirable to contain the radical (for it to also be called an acidolysis nature machine) which an operation of an acid decomposes [radical] and increases solubility in an alkali developer in addition to the radical further shown by the general formula [I] and the repeat structural unit which has an aliphatic-cyclic-hydrocarbon part. Thereby, the improvement effectiveness in sensibility becomes much more remarkable. As such an acidolysis nature machine, above-mentioned -COOR8, -OR8, a 3-oxocyclohexyl radical, or a 2-oxocyclohexyl radical is desirable. Specifically, the repeat structural unit equivalent to the following existing monomers is mentioned.

[0041] For example, t-butyl acrylate, t-butyl methacrylate, t-ethyl acrylate, t-ethyl methacrylate, tetrahydrofuranyl acrylate, tetrahydrofuranyl methacrylate, Tetrahydropyranyl acrylate, tetrahydropyranyl methacrylate, Alkoxy methyl acrylate, alkoxy methyl methacrylate, 1-alkoxy ethyl methacrylate, 3-oxocyclohexyl acrylate, 3-oxocyclohexyl methacrylate, 2-oxocyclohexyl acrylate, 2-oxocyclohexyl methacrylate, etc. can be mentioned.

[0042] The repeat structural unit which has the radical shown by existing acidolysis nature machine / above-mentioned general formula [I] in the content of the repeat structural unit based on the monomer which has such an existing acidolysis nature machine among the above-mentioned resin = 6/1 or less is 3/1 or less desirable still more preferably. Since the effectiveness of this invention will not fully be discovered if this value exceeds 6/1, it is not desirable.

[0043] Although the effectiveness of this invention can repeat the still more nearly following monomers and can make such resin they carry out copolymerization as a unit within limits obtained effectively, it is not limited to these. Thereby, fine tuning of the adhesion to the substrate of the engine performance required of said resin, the solubility over (1) spreading solvent, (2) film-production nature (glass transition point), (3) alkali development property, (4)

***** (relative-degree-of-intimacy aquosity, alkali fusibility radical selection), and (5) unexposed parts and (6) dry-etching resistance ** is attained especially.

[0044] The compound which has one addition polymerization nature unsaturated bond chosen from acrylic ester, methacrylic ester, acrylamides, methacrylamide, an allyl compound, vinyl ether, and vinyl ester as such a copolymerization monomer, for example can be mentioned.

[0045] Specifically For example, acrylic ester, for example, alkyl (carbon atomic number of alkyl group has desirable thing of 1-10) acrylate for example, a methyl acrylate, an ethyl acrylate, and acrylic-acid propyl — Acrylic-acid amyl, acrylic-acid cyclohexyl, acrylic-acid ethylhexyl, Acrylic-acid octyl, acrylic-acid-t-octyl, chlorethyl acrylate, 2-hydroxyethyl acrylate 2, 2-dimethyl hydroxypropyl acrylate, 5-hydroxy pentyl acrylate, trimethylol propane monoacrylate, pentaerythritol monoacrylate, benzyl acrylate, methoxybenzyl acrylate, furfuryl acrylate, tetrahydrofurfuryl acrylate, etc.;

[0046] methacrylic ester (for example, methyl methacrylate —), for example, alkyl (carbon atomic number of alkyl group has desirable thing of 1-10.) methacrylate Ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, Amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, Benzyl methacrylate, KURORU benzyl methacrylate, octyl methacrylate, 2-hydroxyethyl methacrylate, 4-hydroxy butyl methacrylate, 5-hydroxy pentyl methacrylate, 2, and 2-dimethyl-3-hydroxypropyl methacrylate, Trimethylol propane mono-methacrylate, pentaerythritol mono-methacrylate, furfuryl methacrylate, tetrahydrofurfuryl methacrylate, etc.;

[0047] Acrylamides, for example, acrylamide, N-alkyl acrylamide, (As an alkyl group, there are the thing of the carbon atomic numbers 1-10, for example, a methyl group, an ethyl group, a propyl group, butyl, t-butyl, a heptyl radical, an octyl radical, a cyclohexyl radical, a hydroxyethyl radical, etc.) N and N-dialkyl acrylamide (as an alkyl group, there are the thing of the carbon atomic numbers 1-10, for example, a methyl group, an ethyl group, butyl, an isobutyl radical, an ethylhexyl radical, a cyclohexyl radical, etc.) N-hydroxyethyl-N-methylacrylamide, N-2-acetamidoethyl-N-acetyl acrylamide, etc.;

[0048] Methacrylamide, for example, methacrylamide, N-alkyl methacrylamide (as alkyl group, there are thing of carbon atomic numbers 1-10, for example, methyl group, ethyl group, t-butyl, ethylhexyl radical, hydroxyethyl radical, cyclohexyl radical, etc.), N, and N-dialkyl methacrylamide (there are an ethyl group, a propyl group, butyl, etc. as an alkyl group.), N-hydroxyethyl-N-methyl methacrylamide, etc.;

[0049] An allyl compound, for example, allyl ester, allyloxy ethanol (for example, an acetic-acid allyl compound, allyl caproate, a caprylic-acid allyl compound, a lauric-acid allyl compound, a palmitic-acid allyl compound, a stearin acid allyl compound, allyl benzoate, an acetoacetic-acid allyl compound, a lactic-acid allyl compound, etc.), etc.;

[0050] vinyl ether (for example, hexyl vinyl ether —), for example, alkyl vinyl ether Octyl vinyl ether, DESHIRU vinyl ether, ethylhexyl vinyl ether, Methoxy ethyl vinyl ether, ethoxyethyl vinyl ether, KURORU ethyl vinyl ether, The 1-methyl-2, 2-dimethyl propyl vinyl ether, 2-ethyl butyl vinyl ether, Hydroxyethyl vinyl ether, diethylene-glycol vinyl ether, Dimethylaminoethyl vinyl ether, diethylamino ethyl vinyl ether, butylamino ethyl vinyl ether, benzyl vinyl ether, tetrahydrofurfuryl vinyl ether, etc.;

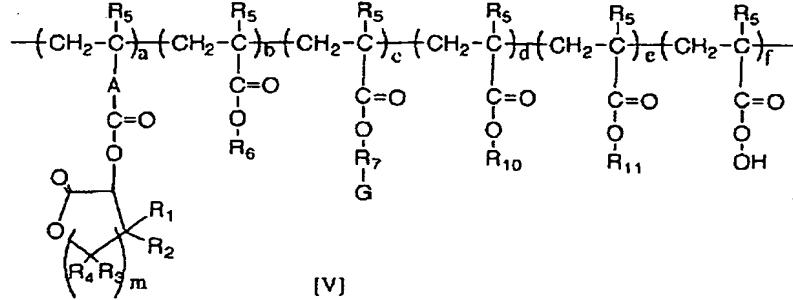
[0051] Vinyl ester, for example, vinyl butyrate, vinyl iso butyrate, vinyl trimethyl acetate, vinyl diethyl acetate, vinyl BARETO, vinyl caproate, vinyl KURORU acetate, vinyl dichloro acetate, vinyl methoxy acetate, vinyl butoxy acetate, vinyl acetoacetate, vinyl lactate, vinyl-beta-phenyl butyrate, vinyl cyclohexyl carboxylate, etc.;

[0052] itaconic-acid dialkyl; (for example, dimethyl MARERETO, dibutylfumarate, etc.) — the dialkyl ester (for example, dimethyl MARERETO, dibutylfumarate, etc.) of a maleic acid or boletic acid, or monoalkyl ester; — there are an acrylic acid, a methacrylic acid, a crotonic acid, an itaconic acid, a maleic anhydride, maleimide, acrylonitrile, a methacrylonitrile, MAREIRO nitril, etc. In addition, what is necessary is just the unsaturated compound of the repeat unit containing the radical which a general formula [I] expresses, and copolymerizable addition polymerization nature. As for the content in the resin of the repeat unit based on the further above monomers, less than [99 mol %] is desirable to the total number of mols of the repeat structural unit which has the repeat structural unit shown by the general formula [I], and an aliphatic-cyclic-hydrocarbon part, and it is less than [80 mol %] preferably [it is more desirable and] to a 90 mol % less or equal and a pan. Since the effectiveness of this invention will not fully be discovered if 99-mol % is exceeded, it is not desirable.

[0053] If it considers as the above-mentioned resin, the following general formulas [V] can show. However, the contents of this invention are not limited to this.

[0054]

[Formula 17]



[0055] R1 ~R7, A, and G are synonymous with the above among the above-mentioned formula [V].

The R 10:3rd class alkyl group, a tetrahydropyranyl group, a tetrahydrofuranyl radical, an alkoxy ethyl group, an alkoxy methyl group, a 3-oxocyclohexyl radical, and a 2-oxocyclohexyl radical are expressed.

R11: Express a methyl group, an ethyl group, a propyl group, an iso-propyl group, or n-butyl.

a: 5-80b:0-70c:0-95d, e, f: Express 0-50 a+d>=5, b+c>=40, a+d>=5, and a+b+c+d+e+f=100 respectively.

[0056] The weight average molecular weight of the resin concerning above-mentioned this invention is 2,000-200,000 preferably. Since development nature will deteriorate or viscosity will become very high if weight average molecular weight exceeds 200,000 not much preferably, since degradation of thermal resistance or dry etching resistance is seen less than by 2,000, the result which is not not much desirable -- film production nature deteriorates -- is produced.

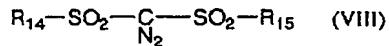
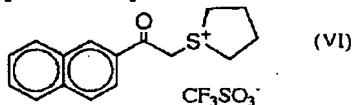
-[0057] The resin concerning this invention is compoundable by the usual approaches including the radical polymerization which makes an azo compound etc. an initiator. The positive type photoresist constituent of this invention mainly contains the above resin and photo-oxide generating agents. The addition in the whole constituent of the above resin is 50 - 97 % of the weight preferably 40 to 99% of the weight among [all] resist solid content.

[0058] Next, the photo-oxide generating agent in the positive type photoresist constituent of this invention is explained. A photo-oxide generating agent needs to fulfill two properties. That is, it is the transparency over (1) exposure light, and photodegradable [for securing (2) resist sensibility (however, when there being no optical bleach nature) / sufficient]. However, although the present condition is that the molecular design guide which fills such a consistent requisite is not clear in, the following examples can be given, for example. That is, the aliphatic series ARUKI sulfonium salt which have the 2-oxocyclohexyl radical of a publication, and N-hydroxysuccinimide sulfonate can be mentioned to JP,7-25846,A, JP,7-28237,A, JP,7-92675,A, and JP,8-27102,A. further --

J.Photospolym.Sci.Technol., Vol 7, No3, and p 423 (1994) etc. -- there is a publication and the compound expressed with the sulfonium salt which can be shown by the following general formula (VI), the JISURU phons which can be shown by the following general formula (VII), and the following general formula (VIII) can be mentioned.

[0059]

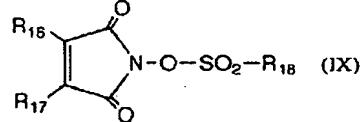
[Formula 18]



[0060] Here, R12-R15 express an alkyl group and an annular alkyl group respectively. these may be mutually the same or may differ. Moreover, the N-hydroxy maleimide sulfonate shown by the following general formula (IX) is suitable.

[0061]

[Formula 19]



[0062] R16 and R17 may be the same, or may differ from each other, and express a hydrogen atom, the alkyl group of 1-6 carbon numbers, or a cycloalkyl radical here. R16 and R17 may join together through an alkylene group, and may form the ring. R18 expresses an alkyl group, a perfluoro-alkyl group, a cycloalkyl radical, or a camphor substitution product. Such N-hydroxy maleimide sulfonate especially is desirable in respect of photosensitivity.

[0063] As an alkyl group of 1-6 carbon numbers in R16 and R17 in the above-mentioned general formula (IX), a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, tert-butyl, n-pentyl radical, and n-hexyl group can be mentioned. Especially, a methyl group, an ethyl group, and a propyl group are desirable, and a methyl group and its ethyl group are still more desirable. As a cycloalkyl radical of six or less carbon numbers, a cyclo propyl group, a cyclopentylic group, and a cyclohexyl radical can be mentioned. They are a cyclopentylic group and a cyclohexyl radical preferably. When R16 and R17 form a ring mutually with an alkylene chain, the case where a cyclohexyl radical, a norbornyl radical, and a tricyclo deca nil radical are formed, for example etc. can be mentioned [*****].

[0064] The alkyl group of 1-20 branched carbon numbers which make the start a methyl group, an ethyl group, the alkyl group of 1-20 carbon numbers of the shape of a straight chain which makes a propyl group the start, an isopropyl group and an isobutyl radical, tert-butyl, and a neopentyl radical as an alkyl group of R18 can be mentioned. It is the straight chain of 1-16 carbon numbers, or the branched alkyl group preferably, and they are the straight chain of 4-15 carbon numbers, or the branched alkyl group still more preferably. As a perfluoro-alkyl group, the perfluoro-alkyl group of 1-20 carbon numbers of the straight chain which makes a trifluoromethyl radical and a pentafluoro ethyl group the start, and the perfluoro-alkyl group of 1-20 branched carbon numbers which make the start a heptafluoro isopropyl group and nona fluoro tert-butyl can be mentioned. They are the straight chain of 1-16 carbon numbers, or the branched perfluoro-alkyl group preferably. A two or more annular alkyl group like the annular alkyl group of the shape of a monocycle like a cyclopentylic group and a cyclohexyl radical as an annular alkyl group, the Di Khalil radical and a norbornyl radical, and a tricyclo deca nil radical can be mentioned.

[0065] The addition in the constituent of such a photo-oxide generating agent has the inside of the total solids of a positive type photoresist constituent, and 0.1 - 20 desirable % of the weight, and it is 1 - 10 % of the weight still more preferably 0.5 to 15% of the weight more preferably.

[0066] In the positive type photoresist constituent of this invention, the following photo-oxide generating agents may be used together besides the above photo-oxide generating agents.

[0067] The addition in the constituent of the photo-oxide generating agent in which the following concomitant use is possible is 2 or less % of the weight in the solid content of the whole positive type photoresist constituent, and its 1 or less % of the weight is still more preferably good. For example S.I.Schlesinger, Photogr.Sci.Eng., 18,387 (1974), T. - S.Bal et al, Polymer, and 21,423 (1980) etc. — the diazonium salt of a publication — U.S. Pat. No. 4,069,055 — said — 4,069,056 A number and ** Re No. 27,992 Japanese Patent Application No. 3-140,140 17 Ammonium salt given in a number etc., D.C.Necker et al, Macromolecules, 2468 (1984), C. S.Wen et al, Teh, Proc.Conf.Rad.Curing ASIA, p478 Tokyo, and Oct (1988), U.S. Pat. No. 4,069,055 — said — 4,069,056 phosphonium salt given in a number etc. — J. V.Crivello et al, Macromolecules, 10 (6), 1307 (1977), Chem.&Eng.News, Nov.28, and p 31 (1988), Europe patent 104,143rd a number and U.S. Pat. No. 339,049 — said — the 410,201st a number — Iodonium salt given in JP,2-150,848,A, JP,2-296,514,A, etc., J. — V.Crivello et al and Polymer J. — 17 and 73 (1985) — J. V.Crivello et al.J.Org.Chem., and 43 and 3055 (1978), W. R.Watt et al, J.Polymer Sci., Polymer Chem.Ed., and 22 and 1789 (1984), J. V.Crivello et al, Polymer Bull., 14,279 (1985), J. V.Crivello et al, Macromolecules, 14 (5), 17 1141 (1981), J.V.Crivello et al, J.PolymerSci., Polymer Chem.Ed., 2877 (1979), Europe patent 370,693rd a number — said — 3,902,114 a number — said — 233,567 a number — said — 297,443 a number — said — 297,442 a number and U.S. Pat. No. 4,933,377 — said — 161,811 a number — said — 410,201 a number — said — 339,049 a number — said — 4,760,013 a number — said — 4,734,444 a number — said — 2,833,827 a number — Germany patent 2,904,626th a number — said — 3,604,580 a number — said — 3,604,581 sulfonium salt given in a number etc. — J. V.Crivello et al, Macromolecules, 10 (6), 1307 (1977), J.V.Crivello et al, J.PolymerSci., Polymer Chem.Ed., 17, and 1047 (1979) etc. — the seleno NIUMU salt of a publication — C. — S.Wen et al, Teh, Proc.Conf.Rad.Curing ASIA, p478 Tokyo, and Oct (1988) etc. — onium salt, such as arsonium salt of a publication, — U.S. Pat. No. 3,905,815, JP,46-4605,B, JP,48-36281,A, JP,55-32070,A, JP,60-239736,A, JP,61-169835,A, JP,61-169837,A, JP,62-58241,A, JP,62-212401,A, An organic halogenated compound given in JP,63-70243,A, JP,63-298339,A, etc., KMeier et al, J.Rad.Curing, 13 (4), 19 26 (1986), T.P.Gilletal, Inorg.Chem., 3007 (1980), D. Astruc, Acc.Chem.Res., 19 (12), and 377 (1896), An organic metal / organic halogenide given in JP,2-161445,A etc., S. Hayase et al, J.Polymer Sci., 25,753 (1987), 23 E.Reichmanis et al, J.Polymer Sci., PolymerChem.Ed., 1 (1985), Q.Q.Zhu et al, J.Photochem., 36, 85; 39,317 (1987), B.Amit et al, Tetrahedron Lett., (24) 2205 (1973), D. H.R.Barton et al, J.Chem Soc., 3571 (1965), P.M.Collins et al, J.Chem.SoC., Perkin I, 1695 (1975), M.Rudinsteinetal, Tetrahedron Lett., (17), 110 1445 (1975), J.W.Walker et al,J.Am.Chem.Soc., 7170 (1988), S.C.Busman et al, J.Imaging Technol., 11 (4), 21 191 (1985), H.M.Houlihan et al, Macromolecules, 2001 (1988), P. M.Collins et al, J.Chem.Soc., Chem.Commun., 532 (1972), S. 18 Hayase et al, Macromolecules, 1799 (1985), E.Reichmanis et al, J.Electrochem.Soc., Solid State Sci.Technol., 130 (6), 21 F.M.Houlihan et al, Macromolecules, 2001 (1988), the Europe patent 0290th and No. 750 — said — 046 and 083 a number — said — 156 and 535 a number — said — 271,851 a number — said — 0,388,343 Number, U.S. Pat. No. 3,901,710 — The photo-oxide generating agent which has o-nitrobenzyl mold protective group of a publication in said 4,181,531 numbers, JP,60-198538,A, JP,53-133022,A, etc., M. TUNOOKA et al, Polymer Preprints Japan, 35 (8), G.Berneretal, J.Rad.Curing, 13 (4), W.J. Mijs et al, Coating Technol., 55 (697), 45 (1983), Akzo, H.Adachi et al, Polymer Preprints, Japan, 37 (3), the Europe patent 0199th and No. 672 — said — 84515 a number — said — 199 and 672 a number — said — 044 and 115 a number — said — No. 0101 or 122 and U.S. Pat. No. 618,564 — said — 4,371,605 a number — said — 4,431,774 a number and JP,64-18143,A — The disulfon compound of a publication can be mentioned to a compound which photodissociates and generates a sulfonic acid, JP,61-166544,A, etc. which are represented by imino sulfonate given in JP,2-245756,A, Japanese Patent Application No. No. 140109 [three to], etc.

[0068] moreover, the radical which generates an acid by such light or the compound which introduced the compound into the principal chain or side chain of a polymer — for example M. E.Woodhouse et al, J.Am.Chem.Soc., and 104 and 5586 (1982), S. P.Pappas et al, J.Imaging Sci., 30 (5), 218 (1986), S.Kondoetal, Makromol.Chem., Rapid Commun., 9,625 (1988), Y. Yamada et al, Makromol.Chem., and 152,153,163 (1972), J. V.Crivello et al, J.PolymerSci., Polymer Chem.Ed., 17, and 3845 (1979), U.S. Pat. No. 3,849,137 and Germany patent 3914407th Number, The compound of a publication can be used for JP,63-26653,A, JP,55-164824,A, JP,62-69263,A, JP,63-146038,A, JP,63-163452,A, JP,62-153853,A, JP,63-146029,A, etc.

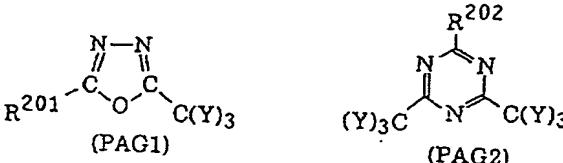
[0069] further — V.N.R.Pillai, Synthesis, (1), 1 (1980), A.Abad et al, Tetrahedron Lett., (47) 4555 (1971), D.H.R.Barton et al, J.Chem.Soc., (C), 329 (1970), U.S. Pat. No. 3,779,778, and Europe patent 126,712nd The compound which generates an acid by the light of a publication can also be used for a number etc.

[0070] In the compound which decomposes by the exposure of the activity beam of light in which the above-mentioned concomitant use is possible, or a radiation, and generates an acid, especially the thing used effectively is explained below.

(1) S-triazine derivative expressed with the oxazole derivative or general formula (PAG2) expressed with the following general formula (PAG1) which the trihalomethyl group permuted.

[0071]

[Formula 20]

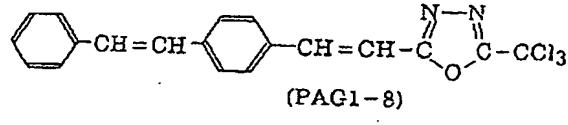
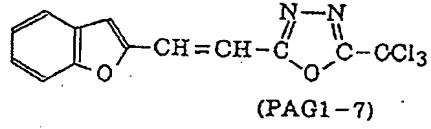
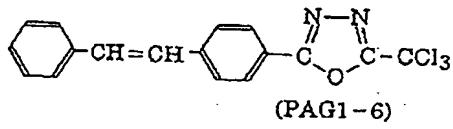
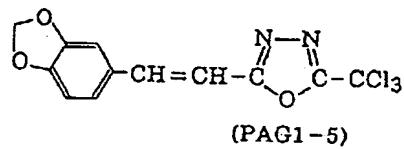
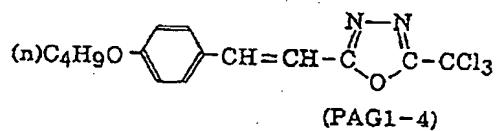
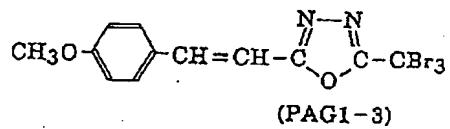
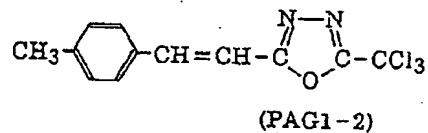
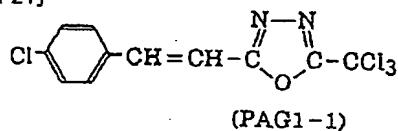


[0072] The inside of a formula, and R201 The aryl group which is not permuted [a permutation or], an alkenyl radical, and R202 The aryl group which is not permuted [a permutation or], an alkenyl radical, an alkyl group, and —

C (Y)3 are shown. Y shows a chlorine atom or a bromine atom. Although the following compounds can specifically be mentioned, it is not limited to these.

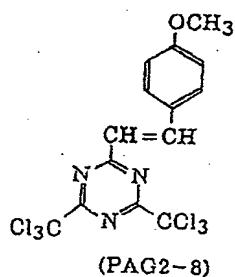
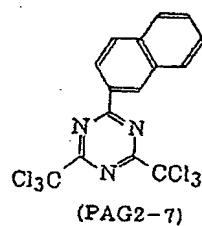
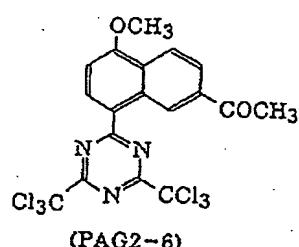
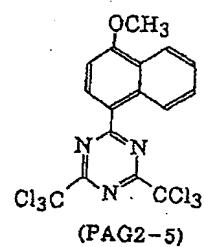
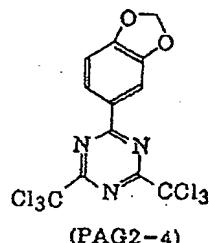
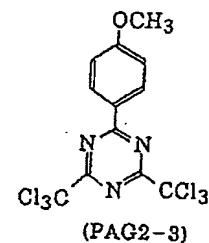
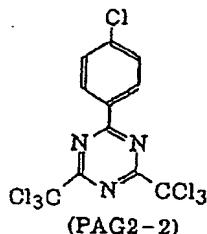
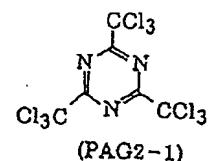
[0073]

[Formula 21]

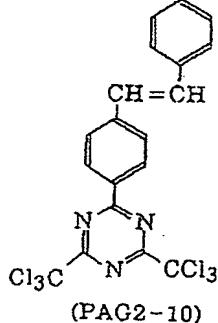
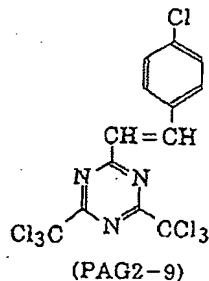


[0074]

[Formula 22]



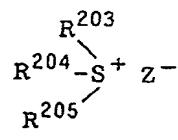
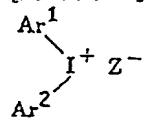
[0075]
[Formula 23]



[0076] (2) Iodonium salt expressed with the following general formula (PAG3), or sulfonium salt expressed with a general formula (PAG4).

[0077]

[Formula 24]



[0078] The inside of a formula, and Ar1 and Ar2 The aryl group which is not permuted [a permutation or] is shown independently respectively. Here, as a desirable substituent, an alkyl group, a halo alkyl group, a cycloalkyl radical, an

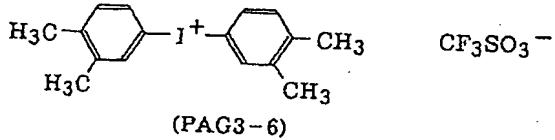
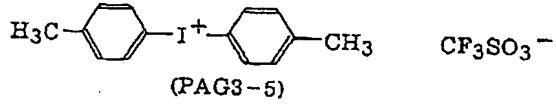
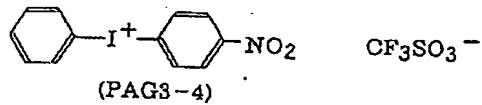
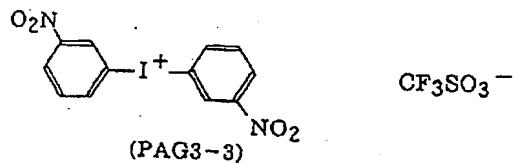
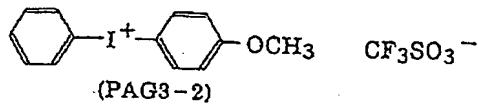
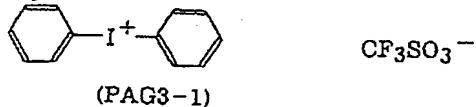
aryl group, an alkoxy group, a nitro group, a carboxyl group, an alkoxy carbonyl group, a HIRONOKISHI radical, a sulphydryl group, and a halogen atom are mentioned.

[0079] R203, R204, and R205 The alkyl group which is not permuted [a permutation or] and an aryl group are shown independently respectively. Preferably, they are the aryl group of carbon numbers 6-14, the alkyl groups of carbon numbers 1-8, and those permutation derivatives. As a desirable substituent, it is the alkoxy group of carbon numbers 1-8, the alkyl group of carbon numbers 1-8, a nitro group, a carboxyl group, a HIRONOKISHI radical, and a halogen atom to an aryl group, and they are the alkoxy group of carbon numbers 1-8, a carboxyl group, and an alkoxy carbonyl group to an alkyl group.

[0080] Z- a **** anion -- being shown -- CF₃SO₃⁻ etc. -- a perfluoro alkane sulfonic-acid anion and a pentafluoro benzenesulfonic acid anion are shown. Moreover, R203, R204, and R205 Two and Ar1, and Ar2 You may join together through each single bond or substituent. Although the compound shown below as an example is mentioned, it is not limited to these.

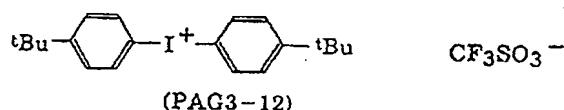
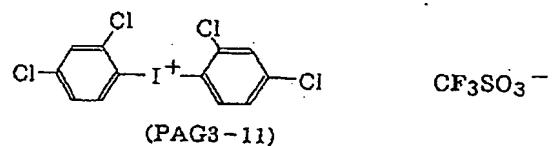
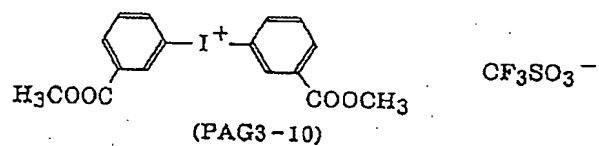
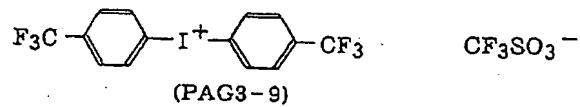
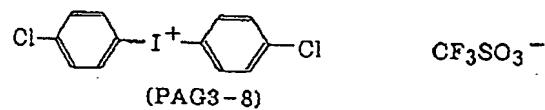
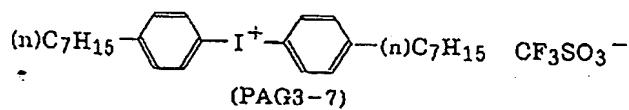
[0081]

[Formula 25]

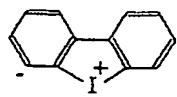


[0082]

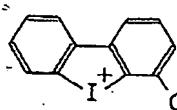
[Formula 26]



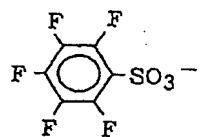
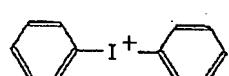
[0083]
[Formula 27]

 CF_3SO_3^-

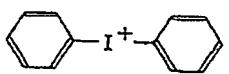
(PAG3-13)

 CF_3SO_3^-

(PAG3-14)



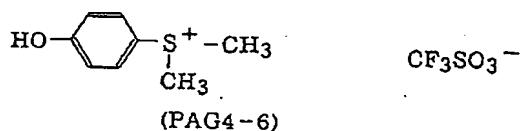
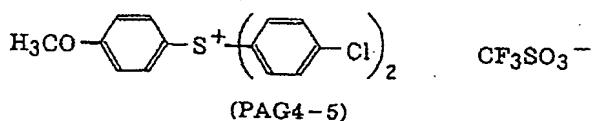
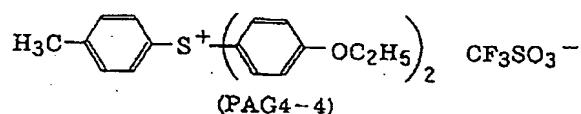
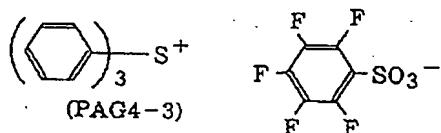
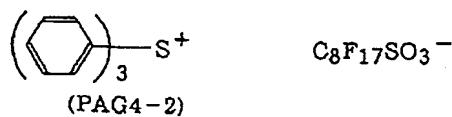
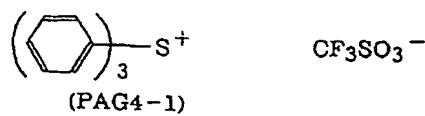
(PAG3-15)

 $\text{C}_8\text{F}_{17}\text{SO}_3^-$

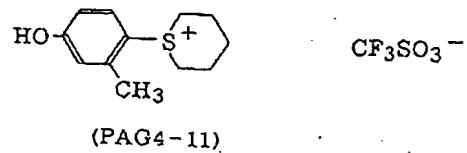
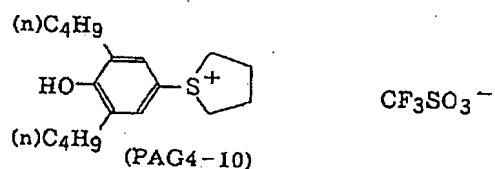
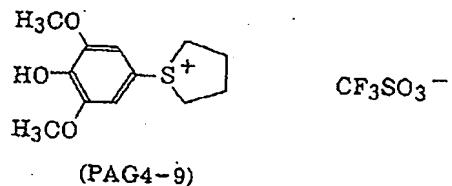
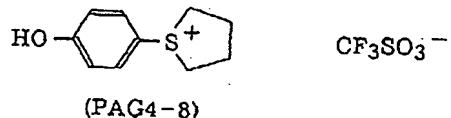
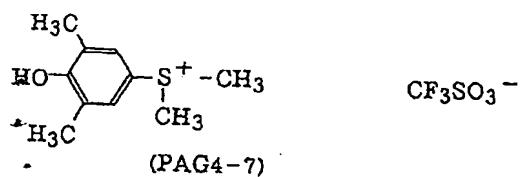
(PAG3-16)

[0084]

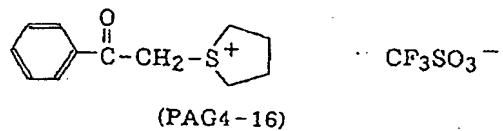
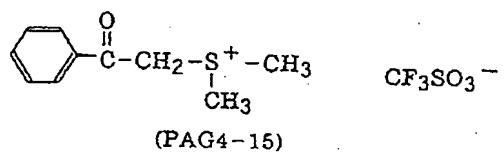
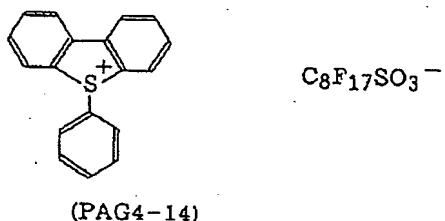
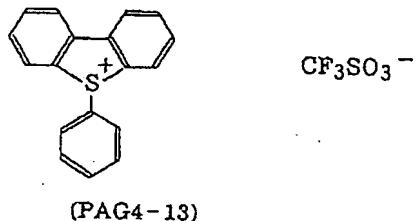
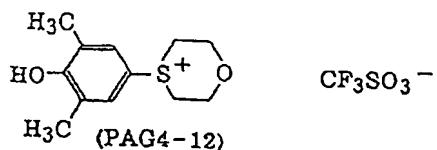
[Formula 28]



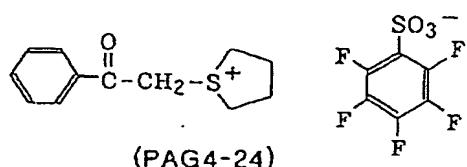
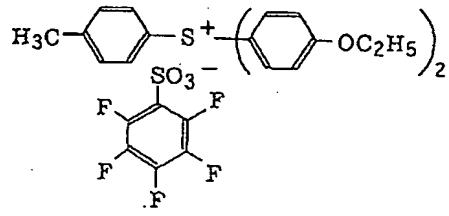
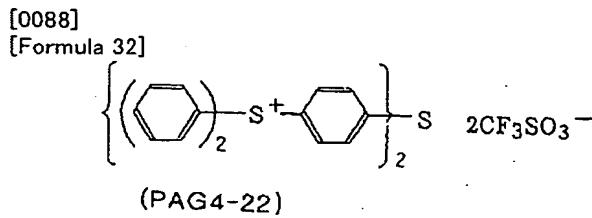
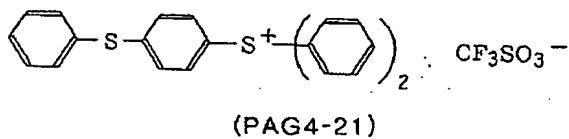
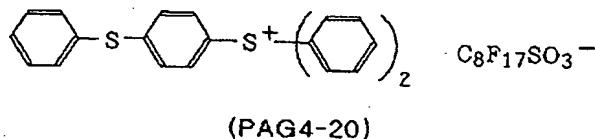
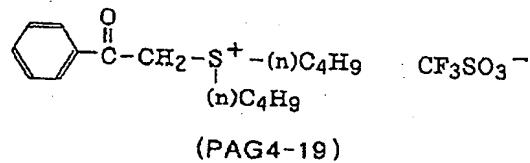
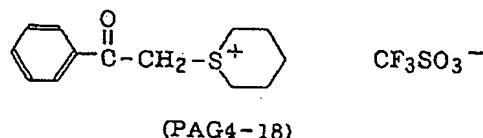
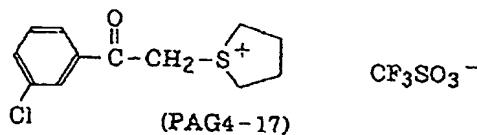
[0085]
 [Formula 29]



[0086]
[Formula 30]



[0087]
[Formula 31]

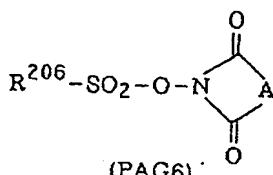
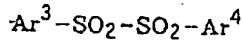


[0089] The above-mentioned onium salt shown by the general formula (PAG3) and (PAG4) is well-known. For example, J.W.Knapczyk et al, J.Am.Chem.Soc., and 91,145 (1969), A. (L.Maycock et al, J.Org.Chem., 35 and 2532, 1970), E. Goethas et al, Bull.Soc.Chem.Belg., and 73 and 546 (1964), H. M.Leicester, J.Ame.Chem.Soc., and 51 and 3587

(1929), J. — V.Crivello et al, J.Polym.Chem.Ed., 18 and 2677 (1980), and U.S. Pat. No. 2,807,648 -- and -- said -- 4,247,473 It is compoundable by the approach of a publication to a number, JP,53-101,331,A, etc.
 (3) The imino sulfonate derivative expressed with the disulfon derivative or general formula (PAG6) expressed with the following general formula (PAG5).

[0090]

[Formula 33]



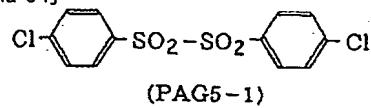
(PAG5)

(PAG6)

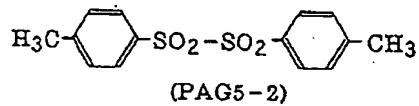
[0091] The inside of a formula, and Ar3 and Ar4 The aryl group which is not permuted [a permutation or] is shown independently respectively. R206 The alkyl group which is not permuted [a permutation or] and an aryl group are shown. A shows the alkylene group which is not permuted [a permutation or], an alkenylene group, and an arylene radical. Although the compound shown below as an example is mentioned, it is not limited to these.

[0092]

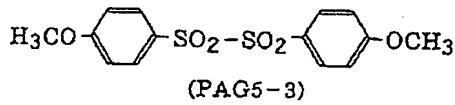
[Formula 34]



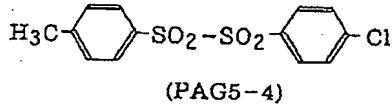
(PAG5-1)



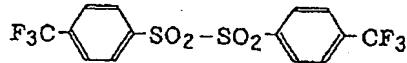
(PAG5-2)



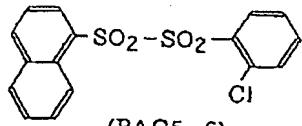
(PAG5-3)



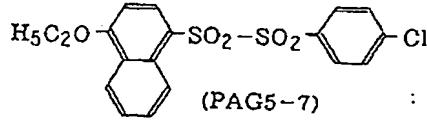
(PAG5-4)



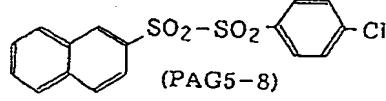
(PAG5-5)



(PAG5-6)



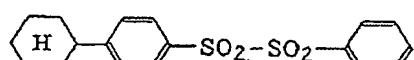
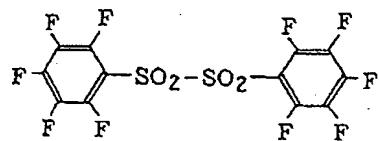
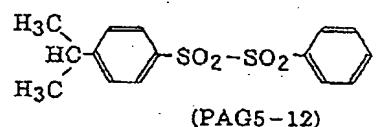
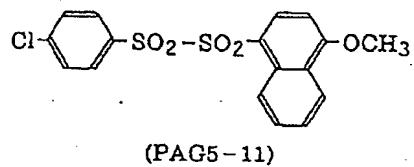
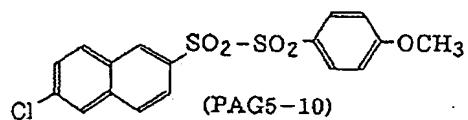
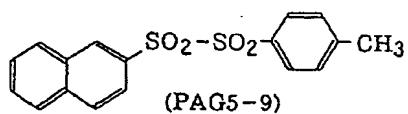
(PAG5-7)



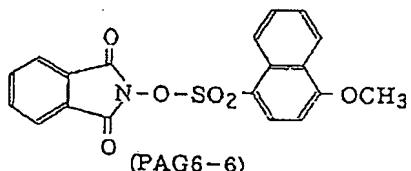
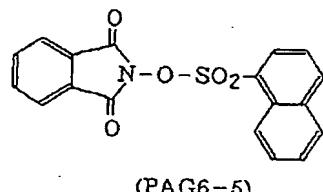
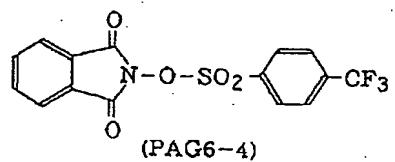
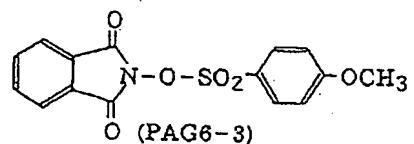
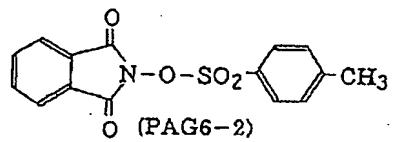
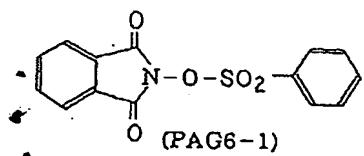
(PAG5-8)

[0093]

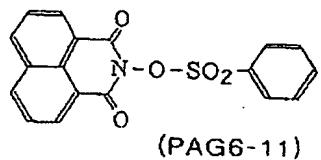
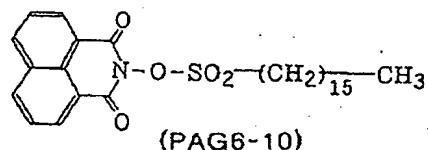
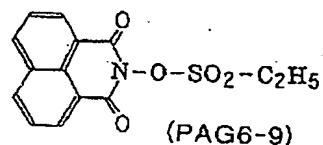
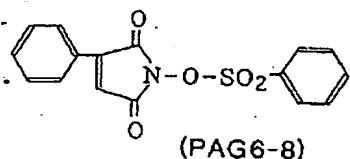
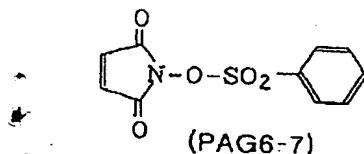
[Formula 35]



[0094]
[Formula 36]

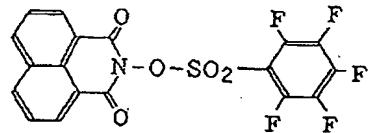
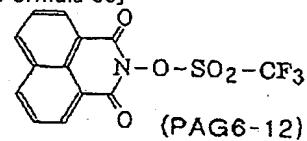


[0095]
[Formula 37]

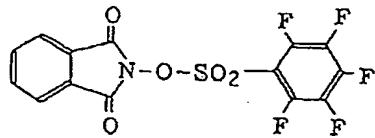


[0096]

[Formula 38]



(PAG6-13)



(PAG6-14)

[0097] To a positive type photoresist constituent, the purpose which raises the alkali solubility of a system, and the glass transition temperature of a system may be adjusted, and the low molecular weight compound of suitable alkali fusibility may be added in order to prevent the film's becoming weak or thermal resistance deteriorating. As this alkali fusibility low molecular weight compound, the compound containing an acidic group can be mentioned to intramolecules, such as a dialkyl sulfonamide compound, and a dialkyl sulfonyl imide ($-SO_2-NH-CO-$) compound, a dialkyl JISURUFO niil imide ($-SO_2-NH-SO_2-$) compound. The content of the low molecular weight compound of this alkali fusibility has 40 or less desirable % of the weight to the above-mentioned binder resin, is 30 or less % of the

weight more preferably, and is 25 or less % of the weight still more preferably.

[0098] The constituent about this invention is good to dissolve and use for a specific solvent. As long as a thing desirable as such a solvent is the organic solvent in which each formed element can fully dissolve, and the solution can form the uniform spreading film by approaches, such as a spin coat method, what kind of solvent is sufficient as it. Moreover, it may be independent, or two or more kinds may be mixed and used. Specifically N-propyl alcohol, isopropyl alcohol, n-butyl alcohol, TASHARU-butyl alcohol, methyl-cellosolve acetate, ethylcellosolve acetate, Propylene glycol monoethyl ether acetate, methyl lactate, Ethyl lactate, acetic-acid 2-methoxy butyl, 2-ethoxyethyl acetate, methyl pyruvate, Pyruvic-acid ethyl, 3-methoxy methyl propionate, 3-methoxy ethyl propionate, N-methyl-2-pyrrolidinone, a cyclohexanone, cyclopentanone, A cyclohexanol, a methyl ethyl ketone, 1,4-dioxane, ethylene glycol monomethyl ether, Although ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether, ethylene glycol mono-isopropyl ether, the diethylene-glycol monomethyl ether, diethylene-glycol wood ether, 2-heptanone, etc. are mentioned Of course, it is not limited only to these.

[0099] Moreover, in the positive type photoresist constituent of this invention, other components, such as a surfactant, coloring matter, a stabilizer, a spreading nature amelioration agent, and a color, may be added further if needed. Such a positive type photoresist constituent of this invention is applied on a substrate, and forms a thin film. The thickness of this paint film has desirable 0.4-1.5 micrometers. As for an ArF excimer laser stepper, what is contained as an exposure means in the range whose exposure wavelength, such as ArF excimer laser stepper exposure, is 170-220nm is desirable especially desirable.

[0100]

[Example] Although an example is shown and this invention is explained concretely hereafter, the contents of this invention are not limited to these.

It dissolved in dichloromethane 500mL and 86g of synthetic methacrylic acids of a synthetic example (1) monomer [II-A-2] was added 4-dimethylaminopyridine 10g. Furthermore, 102g of 2-hydroxy-gamma-butyrolactone was added calmly. This was cooled by the ice bath and dicyclohexylcarbodiimide 25g was added further slowly. After stirring then for 30 minutes, the ice bath was removed, and to the room temperature, the natural temperature up was carried out and it stirred under the room temperature for 3 hours. The fine particles which deposited after reaction termination were carried out the ** exception, and the extract and the oil reservoir which washed after washing and with saturation brine and was obtained with sodium bicarbonate water were further condensed for the obtained filtrate with hydrochloric-acid water 10%. This was refined using the silica gel column chromatography, and monomer [II-A-2] 150g of the purpose was obtained.

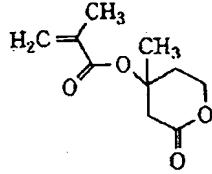
[0101] The methacrylic acid of the example of synthetic composition (1) of a synthetic example (2) monomer [II-C-2] was replaced with light ester HO-MS made from the Kyoeisha chemistry, and also the monomer [II-C-2] was completely compounded by the same actuation.

[0102] The end carboxylic-acid methacrylate which 3-hydroxypropionic acid and the Showa Denko currant MOI were made to react, and was compounded instead of the methacrylic acid of the example of synthetic composition (1) of a synthetic example (3) monomer [II-F-2] was used, and also the monomer [II-F-2] was compounded by the same approach.

[0103] By the synthetic mevalonic lactone and methacrylic-acid chloride of the monomer -1 for synthetic example (4) comparison, the monomer of the following structure was compounded according to the approach of a publication to Journal of Photopolymer Science and Technology Vol.9 and Number 3 (1996) 509.

[0104]

[Formula 39]



[0105]

Composition of synthetic example (5) resin A Tricyclo deca nil methacrylate 22.0g Monomer [II-A-2] 13.6g Methacrylic acid 1.7g THF After dissolving 87g, nitrogen was blown for 30 minutes and reaction mixture was heated at 65 degrees C. V-65 (Wako Pure Chem make) 150mg was added every other hour in 5 steps as a polymerization initiator. After adding the last initiator, heating stirring was carried out as it was for 4 hours. The reaction mixture after heating termination is returned to a room temperature, and it is THF. 200g was added, what diluted reaction mixture was reprecipitated to the mixed solvent of distilled water 4L/methanol 2L, and target resin A was collected as white fine particles. When GPC analysis of the obtained copolymer was performed, weight average molecular weight was 36000 in standard polystyrene conversion.

[0106]

Composition of synthetic example (6) resin B Tricyclo deca nil methacrylate 22.0g Monomer [II-C-2] 25.1g Methacrylic acid 1.7g THF After dissolving 114g, nitrogen was blown for 30 minutes and reaction mixture was heated at 65 degrees C. V-65 (Wako Pure Chem make) 150mg was added every other hour in 5 steps as a polymerization initiator. After adding the last initiator, heating stirring was carried out as it was for 4 hours. The reaction mixture after heating termination is returned to a room temperature, and it is THF. 200g was added, what diluted reaction mixture was reprecipitated to the mixed solvent of distilled water 4L/methanol 2L, and target resin B was collected as white fine particles. When GPC analysis of the obtained copolymer was performed, weight average molecular weight was 37500 in standard polystyrene conversion.

[0107]

Composition of synthetic example (7) resin C Tricyclo deca nil methacrylate 22.0g Monomer [II-F -2] 32.9g Methacrylic acid 1.7g THF After dissolving 133g, nitrogen was blown for 30 minutes and reaction mixture was heated at 65 degrees C. V-65 (Wako Pure Chem make) 150mg was added every other hour in 5 steps as a polymerization initiator. After adding the last initiator, heating stirring was carried out as it was for 4 hours. The reaction mixture after heating termination is returned to a room temperature, and it is THF. 200g was added, what diluted reaction mixture was reprecipitated to the mixed solvent of distilled water 4L/methanol 2L, and target resin C was collected as white fine particles. When GPC analysis of the obtained copolymer was performed, weight average molecular weight was 39000 in standard polystyrene conversion.

[0108]

Composition of synthetic example (8) resin D Tricyclo deca nil methacrylate 17.6g Monomer [II-A -2] 10.2g t-butyl methacrylate 5.7g Methacrylic acid 1.7g THF After dissolving 82g, nitrogen was blown for 30 minutes and reaction mixture was heated at 65 degrees C. V-65 (Wako Pure Chem make) 150mg was added every other hour in 5 steps as a polymerization initiator. After adding the last initiator, heating stirring was carried out as it was for 4 hours. The reaction mixture after heating termination is returned to a room temperature, and it is THF. 200g was added, what diluted reaction mixture was reprecipitated to the mixed solvent of distilled water 4L/methanol 2L, and target resin D was collected as white fine particles. When GPC analysis of the obtained copolymer was performed, weight average molecular weight was 35500 in standard polystyrene conversion.

[0109]

Composition of synthetic example (9) resin E Tricyclo deca nil methacrylate 17.6g Monomer [II-C -2] 18.9g t-butyl methacrylate 5.7g Methacrylic acid 1.7g THF After dissolving 102g, nitrogen was blown for 30 minutes and reaction mixture was heated at 65 degrees C. V-65 (Wako Pure Chem make) 150mg was added every other hour in 5 steps as a polymerization initiator. After adding the last initiator, heating stirring was carried out as it was for 4 hours. The reaction mixture after heating termination is returned to a room temperature, and it is THF. 200g was added, what diluted reaction mixture was reprecipitated to the mixed solvent of distilled water 4L/methanol 2L, and target resin E was collected as white fine particles. When GPC analysis of the obtained copolymer was performed, weight average molecular weight was 37200 in standard polystyrene conversion.

[0110]

Composition of synthetic example (10) resin F Tricyclo deca nil methacrylate 17.6g Monomer [II-F -2] 19.8g t-butyl methacrylate 5.7g Methacrylic acid 1.7g THF After dissolving 105g, nitrogen was blown for 30 minutes and reaction mixture was heated at 65 degrees C. V-65 (Wako Pure Chem make) 150mg was added every other hour in 5 steps as a polymerization initiator. After adding the last initiator, heating stirring was carried out as it was for 4 hours. The reaction mixture after heating termination is returned to a room temperature, and it is THF. 200g was added, what diluted reaction mixture was reprecipitated to the mixed solvent of distilled water 4L/methanol 2L, and target resin F was collected as white fine particles. When GPC analysis of the obtained copolymer was performed, weight average molecular weight was 38500 in standard polystyrene conversion.

[0111]

Composition of the resin G for synthetic example (11) comparison Tricyclo deca nil methacrylate 22.0g Monomer -1 for a comparison 19.9g Methacrylic acid 1.7g THF After dissolving 102g, nitrogen was blown for 30 minutes and reaction mixture was heated at 65 degrees C. V-65 (Wako Pure Chem make) 150mg was added every other hour in 5 steps as a polymerization initiator. After adding the last initiator, heating stirring was carried out as it was for 4 hours. The reaction mixture after heating termination is returned to a room temperature, and it is THF. 200g was added, what diluted reaction mixture was reprecipitated to the mixed solvent of distilled water 4L/methanol 2L, and target resin G was collected as white fine particles. When GPC analysis of the obtained copolymer was performed, weight average molecular weight was 35600 in standard polystyrene conversion.

[0112]

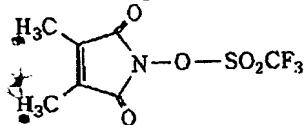
Composition of the resin H for synthetic example (12) comparison Tricyclo deca nil methacrylate 17.6g The monomer -1 for a comparison 12.0g t-butyl methacrylate 5.7g Methacrylic acid 1.7g THF After dissolving 86g, nitrogen was blown for 30 minutes and reaction mixture was heated at 65 degrees C. V-65 (Wako Pure Chem make) 150mg was added every other hour in 5 steps as a polymerization initiator. After adding the last initiator, heating stirring was carried out as it was for 4 hours. The reaction mixture after heating termination is returned to a room temperature, and it is THF. 200g was added, what diluted reaction mixture was reprecipitated to the mixed solvent of distilled water 4L/methanol 2L, and target resin H was collected as white fine particles. When GPC analysis of the obtained copolymer was performed, weight average molecular weight was 34500 in standard polystyrene conversion.

[0113] The synthetic example (13) photo-oxide generating agent (1) was compounded. After dissolving 8g of sodium hydroxides, and 14g of hydroxy amine hydrochlorides in 200ml of distilled water and adding 25g of dimethyl maleic-acid anhydrides, it agitated at the room temperature for 5 hours, and heating churning was continuously carried out at 100 degrees C for 3 hours. Ethyl acetate extracted, after adding hydrochloric-acid water to reaction mixture after reaction termination and making it further saturated with a sodium chloride. Concentration and toluene were added for the extracted ethyl-acetate solution to one third, the actuation which condenses again was repeated and 15g of N-hydroxy maleimide objects was isolated.

[0114] Thus, 4.2g of compound N-hydroxy maleimide objects was dissolved in dichloromethane, and 8.5g of trifluoro methysulfonic acid anhydrides was dropped over 1 hour, ice-cooling. Furthermore, after pyridine 2.8g was dropped over 2 hours, the ice bath was removed and it agitated to the room temperature for 10 hours with temperature up Perilla frutescens (L.) Britton var. crispa (Thunb.) Decne. When distilled water etc. washed reaction mixture after reaction termination, concentration and there were made to carry out crystallization to a hexane and the hexane layer was condensed further, 10g of specified substance was obtained. The structure following by carbon magnetic resonance was checked.

[0115]

[Formula 40]



[0116] [An example and example of a comparison] After dissolving 1.2g of each resin A-H compounded in the above-mentioned synthetic example, and photo-oxide generating agent (1)0.25g in 2-heptanone at a rate of 14 % of the weight of solid content, filtration and a positive type photoresist constituent solution were prepared by the 0.1-micrometer microfilter. The formula is shown in the following table 1.

[0117] (Evaluation trial) The obtained positive type photoresist constituent solution was applied on the silicon wafer using the spin coater, desiccation and about 0.5-micrometer positive type photoresist film were created for 90 seconds at 120 degrees C, and it exposed with the ArF excimer laser (193nm) to it. Heat-treatment after exposure was performed in 90 seconds at 110 degrees C, the rinse was carried out with development and distilled water in 2.38% of tetramethylammonium hydroxide water solution, and the resist pattern profile was obtained.

[0118] [Relative sensibility] Light exposure which can reproduce a 0.5micrometer pattern was made into sensibility, resist sensibility of an example 1 was set to 1, and it asked for the relative sensibility of resists other than example 1 by the degree type. Namely, sensibility of the sensibility / examples 1 other than example 1 [0119] [Pattern profile]: The resist pattern profile obtained above was observed with the scanning electron microscope, and what showed O and T-top configuration for the rectangle thing was evaluated as x.

[0120] [adhesion] (minimum line width of a residual thin line) — : — the resist pattern profile obtained above is observed with a scanning electron microscope, and it remains — it evaluated with the line breadth of a thin line most. That is, although the pattern of line breadth with what [finer] has higher adhesion also remains, finer line breadth will not be able to stick that in which adhesion is conversely inferior by the substrate interface, but a pattern will separate. A result is shown in Table 1.

[0121]

[Table 1]

表1

No	使用した樹脂	相対感度	ループオフ	残存細線の最小線幅
実施例1	A	1. 0	○	0. 29
実施例2	B	0. 9	○	0. 30
実施例3	C	0. 9	○	0. 31
実施例4	D	0. 6	○	0. 28
実施例5	E	0. 5	○	0. 29
実施例6	F	0. 6	○	0. 30
比較例1	G	2. 4	×	0. 59
比較例2	H	1. 7	×	0. 60

[0122] Each example of a comparison includes a problem in respect of relative sensibility, a pattern profile, and adhesion. On the other hand, the examples 1-6 about the positive type photoresist constituent of this invention are in level satisfying about the all. That is, it is suitable for the lithography using far ultraviolet rays including ArF excimer laser exposure.

[0123]

[Effect of the Invention] To the light of the wavelength field of [having explained above] 170nm ~ 220nm, especially this invention is suitable enough, and high sensitivity, is excellent in adhesion, and can offer the positive type photoresist constituent with which a good resist pattern profile is obtained.

[Translation done.]

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CORRECTION OR AMENDMENT

[Kind of official gazette] Printing of amendment by the convention of 2 of Article 17 of Patent Law

[Section partition] The 2nd partition of the 6th section

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[Procedure amendment 1]

[Document to be Amended] Specification

[Item(s) to be Amended] Claim

[Method of Amendment] Modification

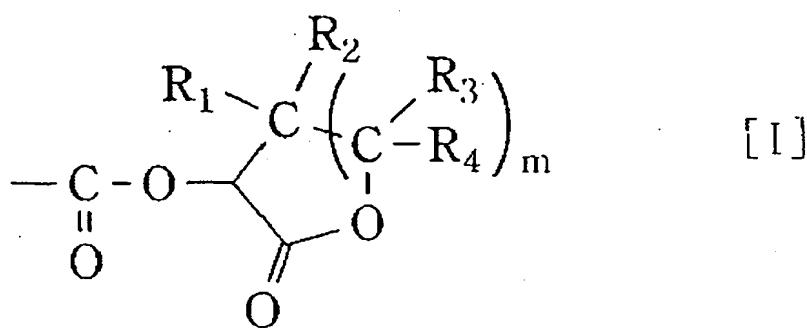
[The contents of amendment]

[Claim(s)]

[Claim 1]

The positive type photoresist constituent characterized by containing the resin which has in intramolecular the ester group expressed with the following general formula [I], and disassembles according to an operation of an acid, and the solubility over an alkali solution increases, and the compound which generates an acid by the exposure of an activity beam of light or a radiation.

[Formula 1]

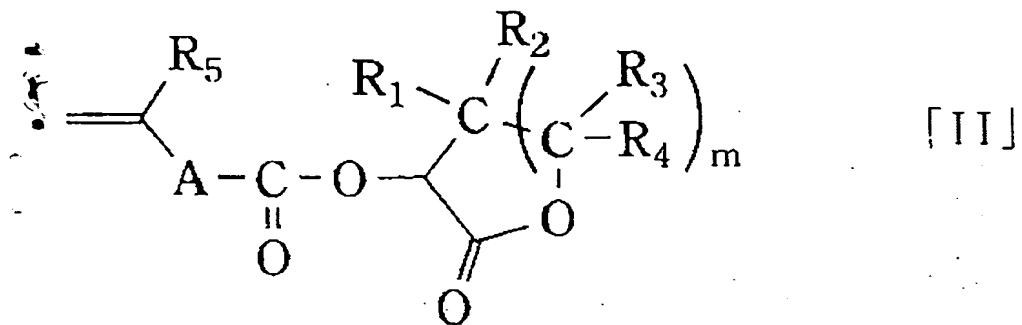


among a formula, R1 -R4 may be the same, or it may differ, and expresses a hydrogen atom or an alkyl group. m expresses 1 or 2.

[Claim 2]

The positive type photoresist constituent according to claim 1 characterized by being resin which disassembles according to an operation of an acid and the solubility over an alkali solution increases, including the repeat structural unit by which said resin is equivalent to the monomer shown by the following general formula [II].

[Formula 2]



(R1 -R4 and m are synonymous with a thing according to claim 1 among a formula.) R5 A hydrogen atom or a methyl group is expressed. A expresses the radical which combined these [one radical chosen from single bond, an alkylene group, a permutation alkylene group, a ether group, a thioether radical, a carbonyl group, an ester group, an amide group, a sulfonamide radical a urethane group, and an urea radical, or] two or more.

[Claim 3]

The positive type photoresist constituent according to claim 1 or 2 characterized by said resin including the repeat structural unit which has an aliphatic-cyclic-hydrocarbon part further.

[Claim 4]

The positive type photoresist constituent according to claim 1 to 3 characterized by said resin including the repeat structural unit which has the radical which an operation of an acid decomposes [radical] further and increases the solubility in the inside of an alkali developer.

[Claim 5]

The positive type pattern formation approach characterized by forming the resist film with a positive type photoresist constituent according to claim 1 to 4, and exposing and developing this resist film.

[Translation done.]